

## PATENT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner  
 US Department of Commerce  
 United States Patent and Trademark  
 Office, PCT  
 2011 South Clark Place Room  
 CP2/5C24  
 Arlington, VA 22202  
 ETATS-UNIS D'AMERIQUE  
 in its capacity as elected Office

<b>Date of mailing</b> (day/month/year) 22 May 2001 (22.05.01)	
<b>International application No.</b> PCT/EP00/08923	<b>Applicant's or agent's file reference</b> H 3609 PCT
<b>International filing date</b> (day/month/year) 13 September 2000 (13.09.00)	<b>Priority date</b> (day/month/year) 22 September 1999 (22.09.99)
<b>Applicant</b> KLEEN, Astrid et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:  
 05 April 2001 (05.04.01)

☐ in a notice effecting later election filed with the International Bureau on:  
 \_\_\_\_\_

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

<b>The International Bureau of WIPO</b> 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Claudio Borton Telephone No.: (41-22) 338.83.38
--	--

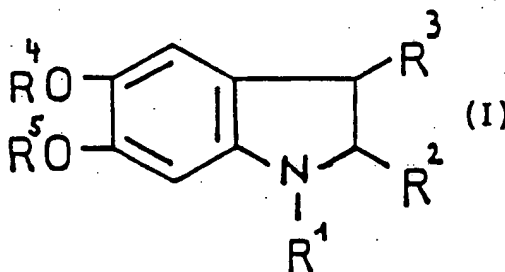
## Oxidation dyes for keratin fibers

This invention relates to the use of indoline derivatives, more particularly 5,6-dihydroxyindolines, as an oxidation dye precursor for the production of oxidation dyes for keratin fibers, more particularly for human hair.

5 Natural hair dyes, so-called melanins, are formed during their biosynthesis by the oxidative polymerization of 5,6-dihydroxyindole. Accordingly, numerous attempts have been made in the past to use 5,6-dihydroxyindole as a reactive dye precursor in the dyeing of hair. Unfortunately, 5,6-dihydroxyindole is extremely unstable both in free form and in the form of its salts in aqueous solution and, in the presence of atmospheric oxygen, very quickly forms insoluble, colored oxidation and polymerization products which can no longer be fixed to the hair. Accordingly, all attempts to use 5,6-dihydroxyindole itself or its salts in dye preparations have led to unsatisfactory and commercially unuseable hair dyes.

A new and surprising possibility has now been found for producing natural hair colors with melanin dyes via a 5,6-dihydroxyindole formed "in situ" without any of the stability problems typical of 5,6-dihydroxyindole.

The present invention relates to the use of indolines corresponding to formula I



in which R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> independently of one another represent hydrogen or C<sub>1-4</sub> alkyl groups or R<sup>4</sup> and R<sup>5</sup> together

with the oxygen atoms to which they are attached may represent an alkylenedioxy group containing 1 to 4 carbon atoms,

5 or salts thereof as oxidation dye precursors for the production of oxidation dyes.

5,6-Dihydroxyindoline, i.e. the indoline derivative corresponding to formula I, in which  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  are hydrogen, is particularly suitable because it forms 5,6-dihydroxyindole and also melanin dye during the oxidation. However, it is also known that derivatives of 5,6-dihydroxyindole form dyes similar to melanin under oxidation conditions. Accordingly, the alkyl-substituted indolines corresponding to formula I, preferably those in which one of the groups  $R^1$ ,  $R^2$  and  $R^3$  is a methyl group and the others are hydrogen, are suitable for use as oxidation dye precursors for the production of storable dye preparations.

By virtue of the chemical similarity of the melanin dyes formed from the indolines to be used in accordance with the invention to the natural melanin dye, the dye preparations produced therewith can be expected to show favorable toxicological and dermatological behavior. Above all, however, particularly natural color tones in the mid-blond to mid-brown range with high fastness to light, mechanical friction, chemical treatment, for example with reducing cold-wave preparations, and to washing with surfactant solutions are obtained.

5,6-Dimethoxyindoline and 5,6-dihydroxyindoline are known from the literature, their production being described, for example, in J. Chem. Soc. (C), 1967, pages 1424 to 1427. The alkyl-substituted indolines corresponding to formula I can be similarly prepared from the correspondingly substituted 5,6-dihydroxyindoles or alkoxyindoles by catalytic hydrogenation. Another process for the production of 5,6-dihydroxyindolines from 5,6-dimethoxy-

indoles by reduction with sodium cyanoborohydride and elimination of the methoxy groups in concentrated hydrochloric acid is described in Journal of Medicinal Chemistry, 1978, Vol. 21, No. 6, page 553.

5           The indolines of formula I to be used in accordance with the invention are preferably used as sole oxidation dye precursors. They may be used in free form or in the form of their salts, preferably as hydrochlorides, hydrobromides, sulfates, phosphates, acetates, propionates,  
10       lactates or citrates.

          However, other known oxidation dye precursors and, optionally, known substantive dyes may also be used together with the indolines corresponding to formula I for modifying the color tones.

15           In particular, it has been found that the indolines corresponding to formula I and also their salts are also eminently suitable for use as color modifiers in oxidation hair dyes containing typical developer compounds.

          Accordingly, the present invention also relates to  
20       hair dyes containing oxidation dye precursors in a carrier, characterized in that they contain indolines corresponding to formula I or salts thereof as color modifiers together with the developer compounds typically used for oxidation hair dyes. The indolines corresponding to formula I modify  
25       the colors obtainable with the developer compounds alone by self-coupling and lead to intensive, brilliant dark-brown to blue-black tones.

          The hair dyes according to the invention preferably contain a mildly basic carrier.

30           The typical developer components used may be any of the compounds known for this purpose. Those of the aromatic or heterocyclic amino compound type are preferred. Suitable developer compounds of this type are, for example, p-phenylenediamine, p-tolylenediamine, 2-chloro-p-phenylenediamine, N-methyl-p-phenylenediamine, N,N-diethyl-p-  
35

phenylenediamine, N-( $\beta$ -hydroxyethyl)-p-phenylenediamine, N,N-dimethyl-p-phenylenediamine, N,N-bis-( $\beta$ -hydroxyethyl)-p-phenylenediamine, 2,5-diaminobenzyl alcohol and other compounds of the type mentioned which may also contain one or more  $\text{NH}_2$  groups, NHR groups or  $\text{NR}_2$  groups, in which R represents  $\text{C}_{1-4}$  alkyl groups or  $\text{C}_{2-4}$  hydroxyalkyl groups, and also p-aminophenols, 1-amino-4-naphthol or tetraaminopyrimidines, for example 2,4,5,6-tetraaminopyrimidine or 2-dimethylamino-4,5,6-triaminopyrimidine, diaminopyrimidines or 1-phenyl-3-carboxamido-4-amino-5-pyrazolone.

Where the indolines corresponding to formula I are used as color modifiers for modifying the color tone of the developer compounds mentioned, they are used in quantities of 0.1 to 10 millimol per 100 g of the hair dye. They are typically used in substantially molar quantities, based on the developer compounds used. Although it has proved to be advisable to use molar quantities, there is no disadvantage in using an excess of individual oxidation dye precursors.

The indoles corresponding to formula I do not have to be individual chemical compounds, instead they may also be mixtures of the indoles corresponding to formula I or their salts to be used in accordance with the invention.

To produce oxidation dyes, the oxidation dye precursors are incorporated in a suitable carrier. Such carriers are, for example, creams, emulsions, gels or even surfactant-containing foaming solutions (shampoos), foam aerosols or other preparations suitable for application to the hair. The carriers in question contain formulation and dyeing aids which increase the stability of the preparations and improve the result of dyeing. Such additives are, primarily, surface-active agents, for example

- soaps, more particularly the alkali metal or alkanol-amine soaps of linear  $\text{C}_{12-18}$  fatty acids, more particularly oleic acid,

- 5       -     anionic surfactants, for example fatty alcohol sulfates and fatty alcohol polyglycol ether sulfates, alkane sulfonates,  $\alpha$ -olefin sulfonates or oleic acid sulfonates, preferably in the form of their alkali metal, ammonium or alkanolammonium salts
- 10       -     cationic surfactants, for example alkyl ( $C_{12-18}$ ) trimethyl ammonium chloride, alkyl ( $C_{12-18}$ ) dimethyl benzyl ammonium salts, cetyl pyridinium chloride, 2-hydroxydodecyl hydroxyethyl dimethyl ammonium chloride
- 15       -     zwitterionic surfactants such as, for example, alkyl ( $C_{12-18}$ ) dimethyl ammonium glycinate, coconut oil acylaminopropyl dimethyl ammonium glycinate or imidazolium betaines
- 20       -     amphoteric surfactants such as, for example, N-dodecylaminoacetic acid, N-cetylaminopropionic acid,  $\gamma$ -laurylaminobutyric acid and
- 25       -     nonionic surfactants, more particularly adducts of 5 to 30 mol ethylene oxide with fatty alcohols, with alkylphenols, with fatty acids, with fatty acid alkanolamides, with fatty acid partial glycerides, with fatty acid sorbitan partial esters or with fatty acid methyl glucoside partial esters, also alkyl glucosides, amine oxides and fatty acid polyglycerol esters.
- 30       Other formulation aids are
- 35       -     water-soluble thickening polymers (hydrocolloids), for example cellulose ethers, such as carboxymethyl cellulose, hydroxyethyl cellulose, methyl cellulose, methyl hydroxypropyl cellulose, starch and starch

ethers, vegetable gums, guar gum, agar agar, alginates, xanthan gum or synthetic water-soluble polymers

- 5       - antioxidants, for example ascorbic acid,  $\text{Na}_2\text{SO}_3$ ,
- buffers, for example ammonium chloride and ammonium sulfates
- 10       - complexing agents, for example 1-hydroxyethane-1,1-diphosphonic acid, nitrilotriacetic acid or ethylenediamine tetraacetic acid or salts thereof,
- 15       - hair-cosmetic auxiliaries, for example water-soluble cationic polymers, protein derivatives, glucose, D-panthenol, cholesterol, vitamins or vegetable extracts,
- 20       - levelling aids, for example urazole, hexahydropyrimidin-2-one, imidazole, 1,2,4-triazole or iodides, for example sodium or potassium iodide.

The hair dyes according to the invention may be applied in the mildly acidic, neutral or mildly alkaline pH range.

25       One preferred embodiment of the invention are hair dyes with a content of oxidation dye precursors in a carrier which contain indolines corresponding to formula I or salts thereof in a quantity of 0.1 to 20 millimol per 100 g hair dye as oxidation dye precursors and, as carrier, a  
30       gel containing 1 to 20% by weight of a soap or an oil-in-water emulsion containing 1 to 25% by weight of a fatty component and 0.5 to 30% by weight of an emulsifier from the group of anionic, nonionic, cationic, zwitterionic or ampholytic surfactants.

35       Preferred neutral or mildly acidic carriers for the

dye preparation are oil-in-water cream emulsions containing  $C_{12-22}$  fatty alcohols, preferably cetyl and stearyl alcohol, as fatty component and nonionic, zwitterionic or cationic emulsifiers, preferably adducts of 10 to 30 mol ethylene oxide with cetyl and stearyl alcohol, which may optionally be adjusted to a pH value of 2.5 to 4 by addition of citric acid or other weak acids.

The indoline of formula I to be used in accordance with the invention is incorporated in this emulsion in a quantity of 2 to 20 millimol per 100 g.

Preferred mildly basic carriers for the dye preparation are gels or oil-in-water emulsions. Suitable gels contain 1 to 20% by weight of a soap, preferably ammonium oleate, and preferably 1 to 10% by weight of a nonionic emulsifier as surface-active agents and 5 to 20% by weight of a  $C_{12-22}$  fatty alcohol as fatty component. Suitable oil-in-water emulsions contain 1 to 25% by weight of a fatty component, preferably a  $C_{12-22}$  fatty alcohol, and 0.5 to 30% by weight of an emulsifier, preferably 1 to 20% by weight of an anionic, nonionic, zwitterionic or ampholytic surfactant.

Basically, the dye may be oxidatively developed with atmospheric oxygen, although it is preferred to use a chemical oxidizing agent, particularly when the hair is not only to be dyed, but also lightened in color at the same time.

Oxidation may be initiated either immediately before application of the dye preparation by mixing with an oxidizing agent or on the hair itself. In the first case, the dye preparation is mixed with an oxidizing agent, preferably with hydrogen peroxide solutions or with hydrogen peroxide adducts with urea, melamine or sodium borate, and applied to the hair after a short contact time, the oxidation process and development of the dye then being completed during the contact time on the hair. This method



of application is extremely easy and is particularly suitable for home use.

Deeper and more brilliant colors are obtained when the dye preparation is initially applied to the hair, left thereon for 10 to 30 minutes and an oxidizing agent preparation is subsequently applied to the hair. Preferred oxidizing agents are hydrogen peroxide solutions or dispersions of potassium or ammonium peroxydisulfate or water-soluble periodates. These dispersions may be similar in composition to the carriers in the form of a cream emulsion described above for neutral or mildly acidic dye preparations. Separate application of the oxidizing agent to the hair requires more care and skill and is therefore preferably done by professional hairdressers.

After a contact time of 15 to 30 minutes, excess dye and oxidizing agent are washed out from the hair. A commercially available anionic shampoo is preferably used for this purpose. If the dye composition already has an adequate surfactant content, it is sufficient to use water.

The following Examples are intended to illustrate the invention without limiting it in any way.

### Examples

#### 1. Mildly acidic dyeing, oxidation on the hair

A dye cream emulsion of the following composition was prepared:

Cetyl/stearyl alcohol (30:70)	6 g
Coconut oil fatty alcohol (C <sub>12-18</sub> )	2 g
Cetyl/stearyl alcohol polyglycol ether (20 EO)	2 g
5,6-Dihydroxyindoline hydrobromide	1 g
Water	89 g

An oxidizing agent dispersion of the following composition was prepared:

	Cetyl/stearyl alcohol (30:70)	6 g
	Coconut oil fatty alcohol (C <sub>12-18</sub> )	2 g
	Cetyl/stearyl alcohol polyglycol ether (20 EO)	2 g
	Ammonium peroxydisulfate	5 g
5	Water	85 g

#### Coloring of hair

The dye cream was applied to 15 cm long strands (weight approx. 2 g) of untreated, standardized 80% grey human hair and left to act thereon for 20 minutes at 25°C.

Without intermediate rinsing, the oxidizing agent dispersion was then applied to the same hair strands and left to act thereon for 20 minutes. The strands were then washed with a typical shampoo, rinsed with water and dried.

A mid-brown color tone and very good masking of the grey in the hair strands were obtained. Fastness to light, fastness to rubbing and resistance to permanent-wave treatment were very good.

#### 2. Mildly alkaline dyeing, oxidation before application to the hair

A dye cream emulsion of the following composition was prepared:

25	Lauryl/myristyl alcohol (70:30)	10 g
	Fatty alcohol (C <sub>12/14</sub> ) ether sulfate (2EO), sodium salt, 28% solution in water	25 g
	Water	60 g
	Na <sub>2</sub> SO <sub>3</sub>	1 g
30	Ammonium sulfate	1 g
	5,6-Dihydroxyindoline hydrobromide	1 g
	Concentrated ammonium solution to pH = 9.5	
	Water	ad 100 g

The constituents were mixed with one another in the above order. After addition of the 5,6-dihydroxyindoline and the ammonium sulfate (buffer), the emulsion was first adjusted to pH 9.5 with concentrated ammonia solution and was then made up with water to 100 g.

Oxidative development of the dye was carried out with 3% hydrogen peroxide solution as oxidizing agent. To this end, 50 g hydrogen peroxide solution (3%) were added to and mixed with 100 g of the emulsion.

The dye cream was applied to approx. 5 cm long strands of standardized, 90% grey, but not especially pretreated human hair and left thereon for 30 minutes at 27°C. On completion of the dyeing process, the hair was rinsed, washed with a typical shampoo and then dried.

A brilliant intensive tone in the dark brown range was obtained.

The hair color was distinguished by very good fastness properties (for example fastness to light, rubbing, cold-wave treatment and washing).

### 3. Use as color modifier together with known developer components

Hair dyes according to the invention were prepared in the form of a hair dye cream emulsion of the following composition:

	Fatty alcohol C <sub>12-18</sub>	10	g
	Fatty alcohol (C <sub>12-14</sub> ) ether sulfate (2 EO), sodium salt, 28% in water	25	g
30	Water	60	g
	Na <sub>2</sub> SO <sub>3</sub>	1	g
	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1	g
	5,6-Dihydroxyindoline hydrobromide	1.74	g
	Developer (component D)	7.5	mmol
35	Concentrated ammonia solution to pH 9.5		
	Water	ad 100	g

Preparation of the cream emulsion, oxidative development and coloring of hair strands were carried out as described in Example 2.

5 The following compounds were successively used as developers (component D)

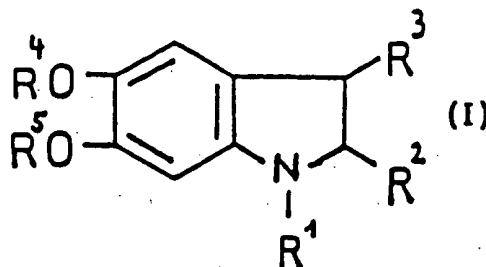
- D1: p-tolylenediamine  
D2: 2-chloro-p-phenylenediamine  
D3: N-methyl-p-phenylenediamine  
10 D4: N,N-diethyl-p-phenylenediamine  
D5: N-( $\beta$ -hydroxyethyl)-p-phenylenediamine  
D6: N,N-dimethyl-p-phenylenediamine  
D7: N,N-bis-( $\beta$ -hydroxyethyl)-p-phenylenediamine  
D8: 2,5-diaminobenzyl alcohol  
15 D9: p-aminophenol  
D10: 1-amino-4-naphthol  
D11: 2,4,5,6-tetraaminopyrimidine

20 The results of the hair dyeing tests are set out in the following Table:

	Hair dye	Developer Component D	Color tone obtained
25	3.1	D1	Black
	3.2	D2	Dark violet
	3.3	D3	Black-violet
	3.4	D4	Black-blue
	3.5	D5	Black-blue
30	3.6	D6	Blue-black
	3.7	D7	Blue-black
	3.8	D8	Dark violet
	3.9	D9	Dark brown
	3.10	D10	Dark brown
35	3.11	D11	Brown-black

## CLAIMS

1. The use of indolines corresponding to formula I



- 10 in which  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  independently of one another represent hydrogen or  $C_{1-4}$  alkyl groups or  $R^4$  and  $R^5$  together with the oxygen atoms to which they are attached may represent an alkylenedioxy group containing 1 to 4 carbon atoms,

- 15 or salts thereof as oxidation dye precursors for the production of oxidation dyes.

2. The use claimed in claim 1, characterized in that, in formula I, the groups  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  are hydrogen or, optionally, one of the groups  $R^1$ ,  $R^2$  and  $R^3$  is a methyl group and the others are hydrogen.

- 20 3. The use claimed in claim 1 or 2, characterized in that the indolines corresponding to formula I or salts thereof are used as color modifiers in oxidation hair dyes containing typical developer compounds.

- 25 4. Hair dyes containing oxidation dye precursors in a carrier, characterized in that indolines of formula I according to claim 1 or 2 or salts thereof are present in a quantity of 0.1 to 20 millimol per 100 g hair dye as oxidation dye precursors while a gel containing 1 to 20% by weight of a soap or an oil-in-water emulsion containing 1 to 25% by weight of a fatty component and 0.5 to 30% by weight of an emulsifier from the group of anionic, non-ionic, cationic or ampholytic surfactants is present as the gel.

- 35 5. Hair dyes as claimed in claim 4, characterized in that

they contain indolines of formula I according to claim 1 or 2 or salts thereof as color modifiers and the developer compounds typically used for oxidation hair dyes.

### Hair-care preparations

This invention relates to hair-treatment preparations containing zwitterionic polymers.

After washing, dyeing or permanent waving, hair often shows unsatisfactory wet and dry combability, in addition to which the curl retention capacity of dry hair is inadequate. To remedy this drawback, either appropriate components have to be added to the hair treatment preparations or the hair has to be subsequently subjected to a separate treatment with these substances which, for this purpose, are normally formulated as a rinse.

Polymeric compounds are frequently used as active substances of the type in question to improve the properties of hair.


Although cationic polymers, such as for example the cellulose derivatives known from US-PSS 3,816,616 and 3,472,840, are capable of distinctly improving wet combability, they only develop unsatisfactory hair-setting and style-holding effects.

The use of zwitterionic polymers containing anionic groups, mostly carboxyl groups, and quaternary ammonium groups in the molecule in hair-treatment preparations is also known. For example, DE-OS 21 50 557 describes the use of polymers of zwitterionic monomers in hair-setting preparations. The use of copolymers of dimethylaminoethyl methacrylate, acrylic acid and methyl methacrylate in hair-setting lotions and shampoos is also known from DE-OS 28 17 369.

These known zwitterionic polymers in hair-treatment and hair-setting preparations have the disadvantage, particularly in formulations with anionic surfactants, that their hair-conditioning and hair-setting properties are gradually lost in the event of prolonged storage. Accord-

ingly, it was proposed in DE-OS 37 08 451 to use zwitter-  
ionic polymers consisting of 30 to 70% monomers containing  
quaternary ammonium groups, 10 to 30% monomeric olefinical-  
ly unsaturated carboxylic acids, 10 to 30% monomeric  
5 olefinically unsaturated carboxylic acid esters and 0 to  
40% monomers containing tertiary amino groups. These  
polymers are highly compatible with anionic and cationic  
surfactants and have good hair-conditioning and style-  
holding properties.

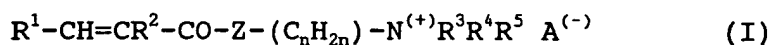
10 Although, therefore, suitable polymers are available  
for obtaining the desired effects on the hair, these  
polymers are made up of at least 3 or 4 monomers. Accord-  
ingly, there is still a need for polymers which, for  
comparable properties, are less complex in structure, i.e.  
15 can be synthesized from a smaller number of different  
monomers.

It has now surprisingly been found that certain  
20  zwitterionic polymers of monomers containing quaternary  
ammonium groups and monomeric carboxylic acids have wet-  
combability-improving, hair-conditioning and style-holding  
properties which, hitherto, have only been achieved with  
polymers of a larger number of different monomers. In  
addition, it is possible with these polymers to formulate  
hair-treatment preparations based on anionic and/or amphi-  
25 teric surfactants which, on the basis of their effect on  
the wet combability of hair, correspond in their perform-  
ance level to known cationic rinses.

Accordingly, the present invention relates to water-  
based hair-treatment preparations containing zwitterionic  
30 polymers, characterized in that the zwitterionic polymers  
are essentially made up of

- A) monomers containing quaternary ammonium groups corre-  
sponding to general formula (I)

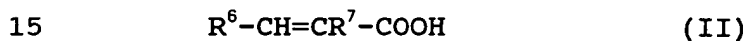




5 in which  $R^1$  and  $R^2$  independently of one another represent hydrogen or a methyl group and  $R^3$ ,  $R^4$  and  $R^5$  independently of one another represent  $C_{1-4}$  alkyl groups, Z is an NH group or an oxygen atom, n is an integer of 2 to 5 and  $A^{(-)}$  is the anion of an organic or inorganic acid

10 and

B) monomeric carboxylic acids corresponding to general formula (II)



in which  $R^6$  and  $R^7$  independently of one another are hydrogen or methyl groups.

20 Suitable starting monomers are, for example, dimethylaminoethyl acrylamide, dimethylaminoethyl methacrylamide, dimethylaminopropyl acrylamide, dimethylaminopropyl methacrylamide and diethylaminoethyl acrylamide in cases where Z is an NH group or dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate and diethylaminoethyl acrylate in cases where Z is an oxygen atom.

25 The monomers mentioned are prepared by known methods of the type described, for example, in US-PS 3,878,247, DE-PS 28 19 735, DE-PS 28 36 520, DE-PS 34 02 599 or CH-PS 464 891.

30 The monomers containing a tertiary amino group are then quaternized in known manner, methyl chloride, dimethyl sulfate or diethyl sulfate being particularly suitable alkylating reagents. The quaternization reaction may take place in aqueous solution or in a solvent. Suitable

processes are described, for example, in DE-OS 33 30 326, DE-OS 25 37 378 or DE-OS 32 44 274.

It is of advantage to use monomers corresponding to formula (I) which are derivatives of acrylamide or methacrylamide. Other preferred monomers are those which contain halide, methoxysulfate or ethoxysulfate ions as counterions. Monomers of formula (I), in which  $R^3$ ,  $R^4$  and  $R^5$  are methyl groups, are also preferred.

Acrylamidopropyl trimethyl ammonium chloride is a particularly preferred monomer of formula (I).

Suitable monomeric carboxylic acids corresponding to formula (II) are acrylic acid, methacrylic acid, crotonic acid and 2-methyl crotonic acid. Acrylic acid or methacrylic acid are preferred, acrylic acid being particularly preferred.

The zwitterionic polymers according to the invention are prepared from monomers corresponding to formulae (I) and (II) by polymerization processes known *per se*. The polymerization may be carried out either in aqueous solution or in aqueous/alcoholic solution. The alcohols used are  $C_{1-4}$  alcohols, preferably isopropanol, which simultaneously act as polymerization regulators. However, other components may be added to the monomer solution as regulators, including for example formic acid or mercaptans, such as thioethanol and thioglycolic acid. The polymerization is initiated by radical-forming compounds. Redox systems and/or thermally decomposing radical formers of the azo compound type, such as for example azoisobutyronitrile, azo-bis-(cyanopentanoic acid) or azo-bis-(amidinopropane)-dihydrochloride, may be used for this purpose. Suitable redox systems are, for example, combinations of hydrogen peroxide, potassium or ammonium peroxodisulfate and tertiary butyl hydroperoxide with sodium sulfite, sodium dithionite or hydroxylamine hydrochloride as reducing component.

The polymerization may be carried out isothermally or under adiabatic conditions, the reaction temperature being variable over the range from 20 to 200°C, depending on the concentrations used, through the heat of polymerization released. The reaction may have to be carried out under the excess pressure spontaneously established. The reaction temperature is preferably in the range from 20 to 100°C.

The pH value during the copolymerization may vary over a wide range. Polymerization is advantageously carried out at low pH values, although it may also be carried out at pH values above the neutral point. On completion of polymerization, the reaction mixture is adjusted to a pH value of 5 to 10 and preferably 6 to 8 with an aqueous base, for example sodium hydroxide, potassium hydroxide or ammonia. Further particulars of the polymerization process can be found in the Examples.

Polymers in which the monomers of formula (I) were present in an excess over the monomers of formula (II) have proved to be particularly effective. In a preferred embodiment of the invention, therefore, the polymers used consist of monomers corresponding to formula (I) and monomers corresponding to formula (II) in a molar ratio of 60:40 to 95:5 and, more particularly, 75:25 to 95:5.

The zwitterionic polymers mentioned are preferably present in the preparations according to the invention in quantities of 0.1 to 10% by weight, based on the preparation as a whole. The polymers are very effective in improving wet combability, even in low concentrations. By contrast, their hair-conditioning and hair-setting effects in most cases are only developed in concentrations above about 1% by weight. Accordingly, it is particularly preferred to use the polymers in quantities of about 1 to 5% by weight.

The zwitterionic polymers according to the invention

are preferably used in water-based preparations containing surface-active compounds. Preferred surface-active compounds are anionic, zwitterionic, amphoteric and/or non-ionic surfactants.

- 5           Suitable anionic surfactants for the hair-treatment preparations according to the invention are any anionic surface-active compounds suitable for use on the human body. They are characterized by a water-solubilizing anionic group such as, for example, a carboxylate, sulfate,  
10   sulfonate or phosphate group and a lipophilic alkyl group containing about 10 to 22 carbon atoms. In addition, glycol ether or polyglycol ether groups, ester, ether and amide groups and also hydroxyl groups may be present in the molecule. Examples of suitable anionic surfactants are the  
15   sodium, potassium and ammonium salts and the mono-, di- and trialkanolammonium salts - containing 2 or 3 carbon atoms in the alkanol group - of
- linear fatty acids containing 10 to 22 carbon atoms (soaps),
  - 20   -   ether carboxylic acids corresponding to the formula  $R-O-(CH_2CH_2O)_x-CH_2-COOH$ , in which R is a linear  $C_{10-22}$  alkyl group and  $x = 0$  or 1 to 10,
  - acyl sarcosides containing 10 to 18 carbon atoms in the acyl group,
  - 25   -   acyl taurides containing 10 to 18 carbon atoms in the acyl group,
  - acyl isethionates containing 10 to 18 carbon atoms in the acyl group,
  - sulfosuccinic acid mono- and dialkyl esters containing  
30   8 to 18 carbon atoms in the alkyl group and sulfosuccinic acid monoalkyl polyethoxyl esters containing 8 to 18 carbon atoms in the alkyl group and 1 to 6 ethoxyl groups.
  - linear alkanesulfonates containing 12 to 18 carbon  
35   atoms,

- linear  $\alpha$ -olefin sulfonates containing 12 to 18 carbon atoms,
- $\alpha$ -sulfofatty acid methyl esters of fatty acids containing 12 to 18 carbon atoms,
- 5 - alkylsulfates and alkyl polyglycol ether sulfates corresponding to the formula  $R-O(CH_2-CH_2O)_x-OSO_3H$ , in which R is a preferably linear alkyl group containing 10 to 18 carbon atoms and  $x = 0$  or 1 to 12,
- 10 - mixtures of surface-active hydroxysulfonates according to DE-OS 37 25 030,
- sulfated hydroxyalkyl polyethylene and/or hydroxy-alkylene propylene glycol ethers according to DE-OS 37 23 254,
- 15 - esters of tartaric acid and citric acid with alcohols which are adducts of about 2 to 15 molecules ethylene oxide and/or propylene oxide with fatty alcohols containing 8 to 22 carbon atoms.

Preferred anionic surfactants are alkyl sulfates and alkyl polyglycol ether sulfates containing 10 to 18 carbon atoms in the alkyl group and up to 12 glycol ether groups in the molecule.

Zwitterionic surfactants are surface-active compounds which contain at least one quaternary ammonium group and at least one  $-COO^{(-)}$  or  $-SO_3^{(-)}$  group in the molecule. Particularly suitable zwitterionic surfactants are the so-called betaines, such as N-alkyl-N,N-dimethyl ammonium glycinate, for example coconut oil alkyl N,N-dimethyl ammonium glycinate, N-acylaminopropyl-N,N-dimethyl ammonium glycinate, for example coconut oil acylaminopropyl-N,N-dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl imidazolines containing 8 to 18 carbon atoms in the alkyl or acyl group and also coconut oil acylaminoethyl hydroxyethyl carboxymethyl glycinate.

Amphoteric surfactants are understood to be surface-active compounds which, in addition to a  $C_{8-18}$  alkyl or acyl

group, contain at least one free amino group and at least one -COOH- or -SO<sub>3</sub>H- group in the molecule and which are capable of forming inner salts. Examples of suitable amphoteric surfactants are N-alkyl glycines, N-alkylamino-  
5 propionic acids, N-alkylaminobutyric acids, N-alkyliminodi-  
propionic acids, N-hydroxyethyl-N-alkylamidopropyl gly-  
cines, N-alkyl taurines, N-alkyl sarcosines, 2-alkylamino-  
propionic acids and alkylaminoacetic acids containing about  
8 to 18 carbon atoms in the alkyl group.

10 Nonionic surfactants are, above all, the adducts of 2  
to 20 mol ethylene oxide with preferably linear alcohols  
containing 12 to 18 carbon atoms, with alkylphenols con-  
taining 8 to 15 carbon atoms in the alkyl group, with fatty  
acids containing 12 to 18 carbon atoms, with fatty acid  
15 partial glycerides, with fatty acid sorbitan partial  
esters, with fatty alkanolamides and with methyl glucoside  
fatty acid esters. Other suitable nonionic surfactants are  
alkyl(oligo)glycosides, alkylamine oxide surfactants and  
fatty acid alkanolamides.

20 Cationic surfactants may also be present in the  
preparations according to the invention providing they are  
compatible with the other components, for example anionic  
surfactants. Such cationic surfactants are known, for  
example, from DE-OS 34 42 175.

25 The preparations according to the invention preferably  
contain surface-active compounds in quantities of 0.1 to  
40% by weight, based on the preparation as a whole.

By virtue of their favorable hair-conditioning and  
hair-setting properties and their compatibility with the  
30 substances typically used in hair-treatment preparations,  
the zwitterionic polymers according to the invention are  
suitable as setting and hair-conditioning components in any  
standard water-based hair-washing and hair-care prepara-  
tions, such as for example shampoos, after-rinses, hair  
35 setting lotions, hair setting gels and water-based color-

ing, permanent-wave and permanent-wave fixing preparations.

Accordingly, the water-based hair-washing and hair-care preparations according to the invention may contain any standard auxiliaries and additives for the particular application envisaged in addition to the compulsory zwitterionic polymers.

For hair rinses, such auxiliaries and additives are, for example, cationic surfactants, more particularly surface-active quaternary ammonium salts, fatty alcohols containing 12 to 22 carbon atoms, fatty acid partial glycerides, cosmetic oil and fatty components and water-soluble polymers having a thickening effect. For hair setting lotions and hair setting gels, the auxiliaries and additives in question are, for example, cationic surfactants, cationic, nonionic or anionic polymers and lower alcohols. Hair-dyeing preparations contain substantive dyes or oxidation dye precursors, anionic or nonionic surfactants, ammonia or alkanolamines and, optionally, antioxidants. Permanent-wave fixing preparations contain an oxidizing agent, for example  $H_2O_2$ ,  $H_2O_2$  adducts or potassium bromate, and also anionic or nonionic surfactants.

The preparations according to the invention preferably have a pH value of 4 to 10 and, more preferably, 5 to 9.

The following Examples are intended to illustrate the invention without limiting it in any way.

#### Examples

1. Preparation of a polymer of acrylamidopropyl trimethyl ammonium chloride and acrylic acid in a molar ratio of 3:1 (polymer P1).

201.17 kg water, 89.59 kg of a 60% by weight aqueous solution of acrylamidopropyl trimethyl ammonium chloride and 6.25 kg acrylic acid were introduced into a reactor

equipped with an impeller stirrer, a heating and cooling system, a reflux condenser and a temperature measuring instrument. A pH value of 3.4 was spontaneously established. The solution was purged with nitrogen and then heated to 60°C. Solutions of 0.06 kg azo-bis-(amidinopropane)-dihydrochloride in 1.00 kg water, 0.024 kg potassium peroxodisulfate in 1,000 kg water and 0.012 kg sodium disulfite in 1,000 kg water were then successively added to the mixture with stirring. Only slight heating occurred. The reaction mixture was heated to 80 - 85°C and kept at that temperature for 4 hours. The polymerization was then terminated. The viscous solution was cooled to 30-40°C and neutralized with 5,000 kg 45% aqueous sodium hydroxide.

The clear colorless polymer solution had the following characteristic data: pH value 6.9, dry matter 20%, product viscosity 13,800 mPa·s, intrinsic viscosity 220 ml/g (in 10% NaCl solution).

## 2. Applications Examples

### 2.1. Hair rinse No. 1

Components	% by weight
Fatty alcohol (C <sub>12-14</sub> ) poly(3EO)glycol ether sulfate, Na salt, 28% aqueous solution	5.0
Coconut oil acyl(C <sub>12-18</sub> )aminopropyl dimethyl glycine, 30% aqueous solution	1.0
Polymer P1 (20% active substance in water)	2.5
Water	ad 100

The rinse is in the form of a cloudy solution. The wet combability of hair treated with this rinse was very good. No adverse effect on the hair or static charging of the hair was observed.



## 2.2 Hair rinse No. 2

Components	% by weight
5 Fatty alcohol (C <sub>12-14</sub> ) poly(3 EO) glycol ether sulfate, Na salt, 28% aqueous solution	5.0
Dehyton® AB 30 <sup>1</sup>	1.0
Polymer P1 (20% active substance in water)	2.5
Water	ad 100

10

<sup>1</sup> Fatty amine derivative of betaine structure, approx.  
30% active substance in water, CTFA name: coco-betaine  
(HENKEL)

15 The rinse is in the form of a cloudy solution. The  
wet combability of hair treated with this rinse was very  
good.

## 2.3 Hair rinse No. 3

20

Components	% by weight
25 Sulfosuccinic acid semiester based on a C <sub>12-14</sub> alkyl poly(3 EO)glycol ether, di- sodium salt (40% active substance in water, CTFA name: disodium laurethsulfosuccinate	0.9
Texapon® K14 S spez. <sup>2</sup>	1.2
Dehyton® AB 30	1.0
Polymer P1 (20% active substance in water)	2.5
Water	ad 100

30

<sup>2</sup> Sodium lauryl myristyl ether sulfate, approx. 30%  
active substance in water (HENKEL)

35 The wet combability of hair treated with this rinse  
was good to very good.

## 2.4 Hair rinse No. 4

	Components	% by weight
5	Sulfosuccinic acid semiester based on a C <sub>12-14</sub> alkyl poly(3 EO)glycol ether, di-sodium salt (40% active substance in water), CTFA name: disodium laurethsulfosuccinate	1.0
	Dehyton® AB 30	7.5
	Polymer P1 (20% active substance in water)	2.5
10	Water	ad 100

The rinse is present in the form of an almost clear solution. The wet combability of hair treated with this rinse was very good.

15

## 2.5 Hair rinse No. 5

	Components	% by weight
	C <sub>16-18</sub> fatty alcohol	3.0
20	Coconut oil acyl(C <sub>12-18</sub> )aminopropyl dimethyl glycine, 30% aqueous solution	8.0
	Fatty alcohol (C <sub>12-14</sub> ) poly(3 EO)glycol ether sulfate, Na salt, 28% aqueous solution	5.0
25	Polymer P1 (20% active substance in water)	2.5
	Water	ad 100

To prepare this hair rinse, the mixture of surfactants and polymer was introduced into the molten fat phase and emulsified therein. The wet combability of hair treated with this rinse was excellent.

30

## 2.6 Hair shampoo No. 1

35	Components	% by weight
	Fatty alcohol (C <sub>12-14</sub> ) poly(3 EO)glycol ether sulfate, Na salt, 28% aqueous solution	50.0
	Coconut oil acyl(C <sub>12-18</sub> )aminopropyl di-	

methyl glycine, 30% aqueous solution	10.0
Polymer P1 (20% active substance in water)	5.0
Water	ad 100

5           The wet combability of hair shampooed with this preparation was excellent.

## 2.7 Hair shampoo No. 2

10	Components	% by weight
	Fatty alcohol (C <sub>12-14</sub> ) poly(3 EO)glycol ether sulfate, Na salt, 28% aqueous solution	45.0
	Coconut oil acyl(C <sub>12-18</sub> )aminopropyl dimethyl glycine, 30% aqueous solution	15.0
15	Akypo® RLM 100 NV <sup>3</sup>	5.0
	Polymer P1 (20% active substance in water)	5.0
	Water	ad 100

20           <sup>3</sup> Aqueous solution of C<sub>12-14</sub> alkyl-O-(CH<sub>2</sub>-CH<sub>2</sub>-O)<sub>10</sub>-CH<sub>2</sub>-COONa, 22% active substance (CHEM-Y)

This shampoo not only freed the hair from soil and grease, it also had a distinct conditioning effect on wet hair and left dry hair with body and volume.

25           To quantify the effect obtained by the polymer, a 15 cm long strand of hair (2 g) was wound onto a glass tube having a external diameter of 1.7 cm, fixed and treated with 0.2 g of the shampoo. The hair strand was then rinsed with water and dried. A measure of the stability of the

30           curl obtained after withdrawal of the glass rod is the curl retention value. The curl retention value is defined as  $[(1-l_x)/(1-l_0)] * 100\%$  where  $l$  is the length of the hair strand (15 cm),  $l_0$  is the length of the hair curl immediately after drying and  $l_x$  is the length of the hair curl after

35           storage for 48 h under constant conditions (30°C/40% relative air humidity) in a drying cabinet. The curls

treated with the shampoo according to the invention had a curl retention value of 94.7% whereas curls treated with a similar shampoo to which polymer P1 had not been added showed a curl retention of only 87.1%.

5

## 2.8 Hair shampoo No. 3

	Components	% by weight
	Texapon® K14 S spez.	15.0
10	Sulfosuccinic acid semiester based on a C <sub>12-14</sub> alkyl polyglycol (3 EO) ether, disodium salt (40% active substance in water), CTFA name: disodium laurethsulfosuccinate	12.0
15	Ethoxylated (9 EO) palm kernel oil fatty acid	1.0
	Alkyl glucoside APG-600	4.0
	Dehyton® CB <sup>5</sup>	9.7
	Polymer P1 (20% active substance in water)	5.0
	Water	ad 100
20		
	<sup>4</sup> Aqueous solution of RO(Z) <sub>x</sub> with Z = glucose, x = 1.4 and R = n-alkyl(C <sub>12-14</sub> ), (50% active substance) (HORIZON)	
25	<sup>5</sup> Aqueous solution of a fatty amine derivative of betaine structure, CTFA name: coco-betaine (approx. 31% active substance, approx. 6.5% NaCl) (HENKEL)	

The shampoo is clear and colorless. This shampoo had an excellent conditioning effect on the hair.

30

## 2.9 Hair shampoo No. 4

	Components	% by weight
35	Sulfosuccinic acid semiester based on a C <sub>12-14</sub> alkyl polyglycol (3 EO) ether, disodium salt (40% active substance in water), CTFA name: disodium laurethsulfosuccinate	12.0
	Ethoxylated (9 EO) palm kernel oil fatty	

	acid	1.0
	Dehyton® CB	10.0
	Eucarol® TA <sup>6</sup>	20.0
	Polymer P1 (20% active substance in water)	1.2
5	Water	ad 100

<sup>6</sup> Aqueous solution of sodium laureth-7-tartrate, 25% active substance (ROL)

10 This clear shampoo was distinguished in particular by an excellent conditioning effect coupled with a good cleaning effect.

#### 2.10 Hair shampoo No. 5

15

Components	% by weight
Sulfosuccinic acid semiester based on a C <sub>12-14</sub> alkyl polyglycol (3 EO) ether, disodium salt (40% active substance in water), CTFA name: disodium laurethsulfosuccinate	15.0
Dehyton® CB	12.0
Alkyl glucoside APG-600	4.0
Polymer P1 (20% active substance in water)	1.2
Water	ad 100

25

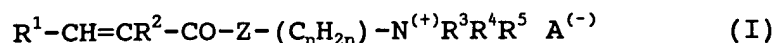
This clear shampoo left the shampooed hair with very good wet combability.

## CLAIMS

1. Water-based hair-treatment preparations containing zwitterionic polymers, characterized in that the zwitterionic polymers are essentially made up of

5

A) monomers containing quaternary ammonium groups corresponding to general formula (I)



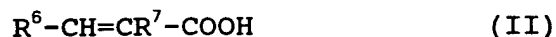
10

in which  $R^1$  and  $R^2$  independently of one another represent hydrogen or a methyl group and  $R^3$ ,  $R^4$  and  $R^5$  independently of one another represent  $C_{1-4}$  alkyl groups, Z is an NH group or an oxygen atom, n is an integer of 2 to 5 and  $A^{(-)}$  is the anion of an organic or inorganic acid

15

and

20 B) monomeric carboxylic acids corresponding to general formula (II)



25

in which  $R^6$  and  $R^7$  independently of one another are hydrogen or methyl groups.

2. Preparations as claimed in claim 1, characterized in that the zwitterionic polymers consist of monomers of type (A) and monomers of type (B) in a molar ratio of 60:40 to 95:5 and, more particularly, 75:25 to 95:5.

30

3. Preparations as claimed in claim 1 or 2, characterized in that, in the monomers of type (A),  $R^3$ ,  $R^4$  and  $R^5$  are methyl groups, Z is an NH group and  $A^{(-)}$  is a halide, methoxysulfate or ethoxysulfate ion.

35

4. Preparations as claimed in any of claims 1 to 3, characterized in that the monomer of type (A) is acrylamidopropyl trimethyl ammonium chloride.
- 5 5. Preparations as claimed in any of claims 1 to 4, characterized in that the monomer of type (B) is acrylic acid.
6. Preparations as claimed in any of claims 1 to 5, characterized in that they contain the zwitterionic polymers in quantities of 0.1 to 10% by weight and more particularly in quantities of 1 to 5% by weight, based on the  
10 preparation as a whole.
7. Preparations as claimed in any of claims 1 to 6, characterized in that they contain at least one surface-active compound selected from the group of anionic, zwitterionic, amphoteric and nonionic surfactants.  
15
8. Preparations as claimed in claim 7, characterized in that they contain the surface-active compounds in quantities of 0.1 to 40% by weight, based on the preparation as a whole.
- 20 9. Preparations as claimed in any of claims 1 to 8, characterized in that they have a pH value of 4 to 10 and, more particularly, 5 to 9.
10. Preparations as claimed in any of claims 1 to 9, characterized in that they are formulated as shampoos or  
25 rinses.
11. The use of the preparations claimed in any of claims 1 to 10 for the treatment of hair.

**Novel Use of UV Filters, Method for Colouring Keratinic Fibres,  
Agents for Realizing this Method**

This invention relates to the use of UV filters for improving the fastness to washing of colors on keratin fibers, to a processes for coloring keratin fibers and to preparations for use in these processes.

Among the various products available for the cosmetic treatment of the human body, formulations for modifying or shading the color of the hair occupy a prominent position. Disregarding blinding preparations which lighten the hair oxidatively by degrading the natural hair dyes, there are largely three types of preparations for changing the color of hair which are of importance in the coloring of hair:

So-called oxidation colorants are used for permanent, intensive colors with corresponding fastness properties. Oxidation colorants normally contain oxidation dye precursors, so-called primary intermediates and secondary intermediates. The primary intermediates form the actual dyes with one another or by coupling with one or more secondary intermediates under the influence of oxidizing agents or atmospheric oxygen. Although oxidation colorants are distinguished by excellent long-lasting coloring results, a mixture of a relatively large number of oxidation dye precursors normally has to be used for natural-looking colors. In many cases, substantive dyes are additionally used for shading. If the dyes formed during color development or directly used have clearly different fastness values (for example UV stability, fastness to perspiration, fastness to washing, etc.), a discernible and hence unwanted change of color can gradually occur. This phenomenon occurs to a greater extent if the hair style has hairs or hair zones damaged to different extents. One example of this are long hairs where the tips exposed for long periods to all kinds of environmental influences are generally damaged to a greater extent than



the relatively freshly regrown hair zones.

Colorants or tints containing substantive dyes as their coloring component are normally used for temporary colors. Substantive dyes are based on dye molecules which are directly absorbed onto the hair and do not require an oxidative process for developing the color. Dyes such as these include, for example, henna which has been used since ancient times for coloring the body and hair. Corresponding colors are generally far more sensitive to shampooing than the oxidative colors so that an often unwanted change of shade or even a visible "decoloration" then occurs very much more quickly.

Finally, a new coloring process has recently attracted considerable interest. In this process, precursors of the natural hair dye melanin are applied to the hair and then form "nature-like" dyes in the hair in the course of oxidative processes. One such process using 5,6-dihydroxyindoline as the dye precursor is described in **EP-B1 530 229**. If preparations containing 5,6-dihydroxyindoline are applied, in particular repeatedly, people with gray hair can be given back their natural hair color. Color development can be carried out with atmospheric oxygen as sole oxidizing agent so that no other oxidizing agent has to be used. In people with originally medium-blond to brown hair, the indoline may be used as sole dye precursor. By contrast, in people with originally red hair and, more particularly, dark to black hair, satisfactory results can often only be obtained by using other dye components as well, more particularly special oxidation dye precursors. In this case, too, the fastness of the colors can be problematical.

Accordingly, there has been no shortage of attempts to improve the fastness of colors on keratin fibers. One development direction is optimization of the dyes themselves or the synthesis of new modified dye molecules. Another development direction is the search for additives for the colorants to increase the fastness of the colors. A known solution to

the problem is to add UV filters to the colorant. These filters are applied to the hair together with the dye during the coloring process so that, in many cases, a distinct increase in the stability of the color to the effect of daylight or artificial light is obtained.

5           It has now surprisingly been found that the fastness to washing of colors on keratin fibers can also be significantly increased by the use of UV filters. Fastness to washing in the context of the present invention is understood to be the retention of the original color in regard to shade and/or intensity when the keratinic fiber is exposed to the repeated  
10   influence of water-based preparations, more particularly surfactant-containing preparations, such as shampoos.

Accordingly, the present invention relates to the use of UV filters for improving the fastness to washing of colors on keratin fibers.

According to the invention, keratin fibers are understood to include  
15   pelts, wool, feathers and in particular human hair.

There are no general restrictions on either the structure or the physical properties of the UV filters to be used in accordance with the invention. On the contrary, any cosmetically usable UV filters of which the absorption maximum lies in the UVA range (315-400 nm), the UVB range  
20   (280-315 nm) or the UVC range (< 280 nm) may be used. UV filters with an absorption maximum in the UVB range, more particularly in the range from about 280 to about 300 nm, are particularly preferred.

The UV filters used in accordance with the invention may be selected, for example, from substituted benzophenones, p-aminobenzoic  
25   acid esters, diphenyl acrylic acid esters, cinnamic acid esters, salicylic acid esters, benzimidazoles and o-aminobenzoic acid esters.

Examples of UV filters suitable for use in accordance with the invention are 4-aminobenzoic acid, N,N,N-trimethyl-4-(2-oxoborn-3-ylidenemethyl)-aniline methyl sulfate, 3,3,5-trimethyl cyclohexyl salicylate  
30   (Homosalate), 2-hydroxy-4-methoxybenzophenone (Benzophenone-3;

Uvinul® M 40, Uvasorb® MET, Neo Heliopan® BB, Eusolex® 4360), 2-phenylbenzimidazole-5-sulfonic acid and potassium, sodium and triethanolamine salts thereof (Phenylbenzimidazole sulfonic acid; Parsol® HS, Neo Heliopan® Hydro), 3,3'-(1,4-phenylenedimethylene)-bis-(7,7-dimethyl-2-oxo-bicyclo-[2.2.1]hept-1-yl methanesulfonic acid) and salts thereof, 1-(4-tert.-butylphenyl)-3-(4-methoxyphenyl)-propane-1,3-dione (Butyl methoxydibenzoylmethane; Parsol® 1789, Eusolex® 9020),  $\alpha$ -(2-oxoborn-3-ylidene)-toluene-4-sulfonic acid and salts thereof, ethoxylated 4-aminobenzoic acid ethyl ester (PEG-25 PABA; Uvinul® P 25), 4-dimethylaminobenzoic acid-2-ethylhexyl ester (Octyl Dimethyl PABA; Uvasorb® DMO, Escalol® 507, Eusolex® 6007), salicylic acid-2-ethyl hexyl ester (Octyl Salicylate; Escalol® 587, Neo Heliopan® OS, Uvinul® O18), 4-methoxycinnamic acid isopentyl ester (Isoamyl p-Methoxycinnamate; Neo Heliopan® E 1000), 4-methoxycinnamic acid-2-ethylhexyl ester (Octyl Methoxycinnamate; Parsol® MCX, Escalol® 557, Neo Heliopan® AV), 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid and its sodium salt (Benzophenone-4; Uvinul® MS 40; Uvasorb® S 5), 3-(4'-methylbenzylidene)-D,L-camphor (4-Methylbenzylidene camphor; Parsol® 5000, Eusolex® 6300), 3-benzylidene camphor (3-Benzylidene camphor), 4-isopropyl benzyl salicylate, 2,4,6-trianilino-(p-carbo-2'-ethylhexyl-1'-oxy)-1,3,5-triazine, 3-imidazol-4-yl acrylic acid and its ethyl ester, polymers of N-((2 and 4)-[2-oxoborn-3-ylidenemethyl]benzyl)-acrylamide, 2,4-dihydroxybenzophenone (Benzophenone-1; Uvasorb® 20 H, Uvinul® 400), 1,1'-diphenylacrylonitrile acid-2-ethylhexyl ester (Octocrylene; Eusolex® OCR, Neo Heliopan® Type 303, Uvinul® N 539 SG), o-aminobenzoic acid menthyl ester (Menthyl Anthranilate; Neo Heliopan® MA), 2,2',4,4'-tetrahydroxybenzophenone (Benzophenone-2; Uvinul® D-50), 2,2'-dihydroxy-4,4'-dimethoxybenzophenone (Benzophenone-6), 2,2'-dihydroxy-4,4'-dimethoxybenzophenone-5-sodium sulfonate and 2-cyano-3,3-diphenylacrylic acid-2'-ethyl hexyl ester. Preferred UV filters are 4-

aminobenzoic acid, N,N,N-trimethyl-4-(2-oxoborn-3-ylidenemethyl)-aniline methyl sulfate, 3,3,5-trimethyl cyclohexyl salicylate, 2-hydroxy-4-methoxybenzophenone, 2-phenylbenzimidazole-5-sulfonic acid and potassium, sodium and triethanolamine salts thereof, 3,3'-(1,4-phenylenedimethylene)-bis-(7,7-dimethyl-2-oxo-bicyclo-[2.2.1]hept-1-yl methanesulfonic acid) and salts thereof, 1-(4-tert.-butylphenyl)-3-(4-methoxyphenyl)-propane-1,3-dione,  $\alpha$ -(2-oxoborn-3-ylidene)-toluene-4-sulfonic acid and salts thereof, ethoxylated 4-aminobenzoic acid ethyl ester, 4-dimethylaminobenzoic acid-2-ethylhexyl ester, salicylic acid-2-ethyl hexyl ester, 4-methoxycinnamic acid isopentyl ester, 4-methoxycinnamic acid-2-ethylhexyl ester, 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid and its sodium salt, 3-(4'-methylbenzylidene)-D,L-camphor, 3-benzylidene camphor, 4-isopropyl benzyl salicylate, 2,4,6-trianilino-(p-carbo-2'-ethylhexyl-1'-oxy)-1,3,5-triazine, 3-imidazol-4-yl acrylic acid and its ethyl ester, polymers of N-[(2 and 4)-[2-oxoborn-3-ylidenemethyl]benzyl]-acrylamide. According to the invention, 2-hydroxy-4-methoxybenzophenone, 2-phenylbenzimidazole-5-sulfonic acid and potassium, sodium and triethanolamine salts thereof, 1-(4-tert.butylphenyl)-3-(4-methoxyphenyl)-propane-1,3-dione, 4-methoxycinnamic acid-2-ethylhexyl ester and 3-(4'-methylbenzylidene)-D,L-camphor are most particularly preferred.

UV filters with a molar extinction coefficient at the absorption maximum of more than 15,000 and more particularly above 20,000 are preferred.

It has also been found that, with structurally similar UV filters, the water-insoluble compound in many cases is more effective in the context of the teaching according to the invention than water-soluble compounds which are distinguished from it by one or more additional ionic groups. In the context of the invention, water-insoluble UV filters are UV filters of which no more than 1% by weight and, more particularly, no more than

0.1% by weight dissolves in water at 20°C. In addition, at least 0.1% by weight and, more particularly, at least 1% by weight of these compounds should dissolve in typical cosmetic oil components at room temperature. Accordingly, it may be preferable in accordance with the invention to use  
5 water-insoluble UV filters.

In another embodiment of the invention, preferred UV filters contain a cationic group, more particularly a quaternary ammonium group.

These UV filters have the general structure U - Q where the structural moiety U is a UV-absorbing group. In principle, this group may  
10 be derived from the known, cosmetically usable UV filters mentioned above in which one group, generally a hydrogen atom, of the UV filter is replaced by a cationic group Q, more particularly with a quaternary amino function.

Examples of compounds from which the structural moiety U may be derived are

- 15 - substituted benzophenones,
- p-aminobenzoic acid esters,
- diphenylacrylic acid esters,
- cinnamic acid esters,
- salicylic acid esters,
- 20 - benzimidazoles and
- o-aminobenzoic acid esters.

According to the invention, preferred structural moieties U are derived from cinnamic acid amide or from N,N-dimethylaminobenzoic acid amide.

25 In principle, the structural moieties U may be selected so that the absorption maximum of the UV filters can lie both in the UVA (315-400 nm) range and in the UVB (280-315 nm) range or in the UVC (< 280 nm) range. UV filters with an absorption maximum in the UVB range, more especially in the range from about 280 to about 300 nm, are particularly preferred.

30 In addition, the structural moiety U may preferably be selected -

even in dependence upon the structural moiety Q - so that the molar extinction coefficient of the UV filter at the absorption maximum is above 15,000 and more particularly above 20,000.

5 The structural moiety Q preferably contains a quaternary ammonium group as the cationic group. In principle, this quaternary ammonium group may be directly attached to the structural moiety U so that the structural moiety U represents one of the four substituents of the positively charged nitrogen atom. However, one of the four substituents at the positively charged nitrogen atom is preferably a group, more particularly an alkylene  
10 group containing 2 to 6 carbon atoms, which acts as a link between the structural moiety U and the positively charged nitrogen atom.

The group Q advantageously has the general structure  $-(CH_2)_xN^+R^1R^2R^3X^-$ , where x is an integer of 1 to 4,  $R^1$  and  $R^2$  independently of one another represent  $C_{1-4}$  alkyl groups,  $R^3$  is a  $C_{1-22}$  alkyl group or a benzyl  
15 group and  $X^-$  is a physiologically compatible anion. In this general structure, x is preferably the number 3,  $R^1$  and  $R^2$  each represent a methyl group and  $R^3$  is either a methyl group or a saturated or unsaturated, linear or branched hydrocarbon chain containing 8 to 22 and more particularly 10 to 18 carbon atoms.

20 Physiologically compatible anions are, for example, inorganic anions, such as halides, more particularly chloride, bromide and fluoride, sulfate ions and phosphate ions, and organic anions, such as lactate, citrate, acetate, tartrate, methosulfate and tosylate.

25 Two preferred UV filters containing cationic groups are the compounds obtainable as commercial products cinnamic acid amidopropyl trimethylammonium chloride (Incroquat® UV-283) and dodecyl dimethylaminobenzamidopropyl dimethylammonium tosylate (Escalol® HP 610).

30 The teaching according to the invention does of course also encompass the use of a combination of several UV filters. In this

embodiment, a combination of at least one water-insoluble UV filter with at least one UV filter containing a cationic group is preferred.

The UV filters are present in the compositions used in accordance with the invention in quantities of normally 0.1 to 5% by weight and preferably 0.4 to 2.5% by weight, based on the composition as a whole.

The effect of the UV filters according to the invention may be further increased by using them in combination with at least one mono-, di- or oligosaccharide. Preferred saccharides are glucose, galactose, fructose, mannose, fruit sugar and lactose. Glucose is particularly preferred.

The saccharides are present in the compositions according to the invention in quantities of 0.1 to 10% by weight and more particularly 1 to 3% by weight, based on the particular formulation.

The effect of the UV filters according to the invention may also be significantly increased by using them in combination with a spreading agent.

Spreading agents in the context of the invention are substances which produce a uniform distribution of active principles, more particularly UV filters, on the surface of the keratin fibers.

Preferred spreading agents are oil components.

Oil components suitable for the purposes of the invention are, in principle, any water-insoluble oils and fatty compounds and mixtures thereof with solid paraffins and waxes. According to the invention, water-insoluble substances are defined as substances of which less than 0.1% by weight dissolves in water at 20°C. The melting point of the individual oil or fatty components is preferably below about 40°C. Oil and fatty components which are liquid at room temperature, i.e. below 25°C, can be particularly preferred for the purposes of the invention. However, where several oil and fatty components and optionally solid paraffins and waxes are used, it is generally sufficient if the mixture of the oil and fatty components and optionally paraffins and waxes satisfies these

requirements.

A preferred group of oil components are vegetable oils. Examples of such oils are sunflower oil, olive oil, soya oil, rapeseed oil, almond oil, jojoba oil, orange oil, wheatgerm oil, peach kernel oil and the liquid  
5 fractions of coconut oil.

However, other triglyceride oils, such as the liquid fractions of bovine tallow, and synthetic triglyceride oils are also suitable.

Another group of compounds particularly preferred for use as oil components in accordance with the invention are liquid paraffin oils and  
10 synthetic hydrocarbons and di-n-alkyl ethers containing a total of 12 to 36 carbon atoms and, more particularly, 12 to 24 carbon atoms, such as for example di-n-octyl ether, di-n-decyl ether, di-n-nonyl ether, di-n-undecyl ether, di-n-dodecyl ether, n-hexyl-n-octyl ether, n-octyl-n-decyl ether, n-decyl-n-undecyl ether, n-undecyl-n-dodecyl ether and n-hexyl-n-undecyl  
15 ether and ditert.butyl ether, diisopentyl ether, di-3-ethyldecyl ether, tert.butyl-n-octyl ether, isopentyl-n-octyl ether and 2-methylpentyl-n-octyl ether. The compounds 1,3-di-(2-ethylhexyl)-cyclohexane and di-n-octyl ether obtainable as commercial products (Cetiol® S and Cetiol® OE, respectively) can be preferred.

20 Other oil components suitable for use in accordance with the invention are fatty acid and fatty alcohol esters. The monoesters of fatty acids with alcohols containing 3 to 24 carbon atoms are preferred. This group of substances are products of the esterification of fatty acids containing 8 to 24 carbon atoms such as, for example, caproic acid,  
25 caprylic acid, 2-ethylhexanoic acid, capric acid, lauric acid, isotridecanoic acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselic acid, linoleic acid, linolenic acid, elaeostearic acid, arachic acid, gadoleic acid, behenic acid and erucic acid and the technical mixtures thereof obtained, for example, in the pressure  
30 hydrolysis of natural fats and oils, in the reduction of aldehydes from



Roelen's oxosynthesis or in the dimerization of unsaturated fatty acids with alcohols such as, for example, isopropyl alcohol, caproic alcohol, caprylic alcohol, 2-ethylhexyl alcohol, capric alcohol, lauryl alcohol, isotridecyl alcohol, myristyl alcohol, cetyl alcohol, palmitoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, linolyl alcohol, linolenyl alcohol, elaeostearyl alcohol, arachyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol and brassidyl alcohol and the technical mixtures thereof obtained, for example, in the high-pressure hydrogenation of technical methyl esters based on fats and oils or aldehydes from Roelen's oxosynthesis and as monomer fraction in the dimerization of unsaturated fatty alcohols. According to the invention, isopropyl myristate, isononanoic acid C<sub>16-18</sub> alkyl ester (Cetiol® SN), stearic acid-2-ethylhexyl ester (Cetiol® 868), cetyl oleate, glycerol tricaprylate, cocofatty alcohol caprate/caprylate and n-butyl stearate are particularly preferred.

Other oil components suitable for use in accordance with the invention are dicarboxylic acid esters, such as di-n-butyl adipate, di-(2-ethylhexyl)-adipate, di-(2-ethylhexyl)-succinate and diisotridecyl acetate, and diol esters, such as ethylene glycol dioleate, ethylene glycol diisotridecanoate, propylene glycol di-(2-ethylhexanoate), propylene diisostearate, propylene glycol dipelargonate, butanediol diisostearate and neopentyl glycol dicaprylate, and also complex esters, for example diacetyl glycerol monostearate.

In addition, fatty alcohols containing 8 to 22 carbon atoms may be used as spreading agents acting in accordance with the invention. The fatty alcohols used in accordance with the invention may be saturated or unsaturated and linear or branched. Examples of fatty alcohols suitable for use in accordance with the invention are decanol, octanol, octenol, dodecenol, decenol, octadienol, dodecadienol, decadienol, oleyl alcohol, erucyl alcohol, ricinoyl alcohol, stearyl alcohol, isostearyl alcohol, cetyl

alcohol, lauryl alcohol, myristyl alcohol, arachidyl alcohol, capryl alcohol, capric alcohol, linoleyl alcohol, linolenyl alcohol and behenyl alcohol and Guerbet alcohols thereof (this list is purely exemplary and is not intended to limit the invention in any way). However, the fatty alcohols emanate from

5 preferably natural fatty acids, normally being obtained from the esters of the fatty acids by reduction. According to the invention, it is also possible to use the fatty alcohol cuts which are produced by reduction of naturally occurring triglycerides, such as beef tallow, palm oil, peanut oil, rapeseed oil, cottonseed oil, soybean oil, sunflower oil and linseed oil, or fatty acid

10 esters formed from the transesterification products thereof with corresponding alcohols and which therefore represent a mixture of different fatty alcohols.

Finally, other oil components preferably used for the purposes of the invention are silicone oils, more particularly dialkyl and alkylaryl siloxanes

15 such as, for example, dimethyl polysiloxane and methylphenyl polysiloxane and alkoxyated and quaternized analogs thereof. Examples of such silicones are the products marketed by Dow Corning under the names of DC 190, DC 200 and DC 1401 and the commercial products DC 344 and DC 345 of Dow Corning, Q2-7224 (manufacturer: Dow Corning; a stabilized

20 trimethyl silyl amodimethicone), Dow Corning® 929 emulsion (containing a hydroxylamino-modified silicone which is also known as amodimethicone), SN-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) and Abil® Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquaternary polydimethyl siloxanes, quaternium-80).

25 The total quantity of spreading agents in the preparations used in accordance with the invention is normally 0.5 to 20% by weight, based on the preparation as a whole. According to the invention, quantities of 1 to 5% by weight are preferred.

The positive effect of the spreading agents is enhanced if they are

30 used together with cationic or anionic surfactants.

Examples of the cationic surfactants suitable for use in accordance with the invention are, in particular, quaternary ammonium compounds. Preferred quaternary ammonium compounds are ammonium halides, such as alkyl trimethyl ammonium chlorides, dialkyl dimethyl ammonium chlorides and trialkyl methyl ammonium chlorides, for example cetyl trimethyl ammonium chloride, stearyl trimethyl ammonium chloride, distearyl dimethyl ammonium chloride, lauryl dimethyl ammonium chloride, lauryl dimethyl benzyl ammonium chloride and tricetyl methyl ammonium chloride. Alkyl amidoamines, particularly fatty acid amidoamines, such as the stearyl amidopropyl dimethyl amine obtainable as Tego Amid® S 18, are further distinguished by their ready biodegradability. Quaternary ester compounds, so-called "esterquats", such as the methyl hydroxyalkyl dialkoyloxyalkyl ammonium methosulfates marketed under the trade name of Stepantex® and the corresponding products marketed under the name of Dehyquart® are also readily biodegradable. One example of a quaternary sugar derivative suitable for use as a cationic surfactant is the commercially available product Glucquat® 100 (CTFA name: Lauryl Methyl Gluceth-10 Hydroxypropyl Dimonium Chloride).

Suitable anionic surfactants are any anionic surface-active substances suitable for use on the human body. Such substances are characterized by a water-solubilizing anionic group such as, for example, a carboxylate, sulfate, sulfonate or phosphate group and a lipophilic alkyl group containing around 10 to 22 carbon atoms. In addition, glycol or polyglycol ether groups, ether, amide and hydroxyl groups and generally ester groups may also be present in the molecule. Preferred anionic surfactants are alkyl sulfates, alkyl polyglycol ether sulfates and ether carboxylic acids containing 10 to 18 carbon atoms in the alkyl group and up to 12 glycol ether groups in the molecule and, in particular, salts of saturated and in particular unsaturated C<sub>8-22</sub> carboxylic acids, such as oleic acid, stearic acid, isostearic acid and palmitic acid. The anionic surfactants

which contain at least one carboxylate group are particularly preferred.

It has been found that the effectiveness of the UV filters in increasing fastness to washing is evident both when the UV filter is applied to the keratin fibers together with the actual colorant and when the UV filter  
5 is applied with a separate formulation immediately after coloring.

The present invention also relates to a process for coloring keratin fibers in the usual way with a colorant, characterized in that the colorant additionally contains a UV filter to increase the fastness of the color to washing. In the process according to the invention, too, the human hair  
10 represents the preferred type of keratin fiber.

The are no basic restrictions to the composition of the colorant.

Suitable dye (precursors) include

- oxidation dye precursors of the primary and secondary intermediate type,
- 15 • natural and synthetic substantive dyes and
- precursors of "nature-like" dyes, such as indole and indoline derivatives

and mixtures of representatives of one of more of these groups.

Oxidation dye precursors of the primary intermediate type are  
20 normally primary aromatic amines with another free or substituted hydroxy or amino group in the para or ortho position, diaminopyridine derivatives, heterocyclic hydrazones, 4-aminopyrazolone derivatives and 2,4,5,6-tetraaminopyrimidine and derivatives thereof. According to the invention, preferred primary intermediates are p-phenylenediamine, p-  
25 toluylenediamine, p-aminophenol, o-aminophenol, 1-(2'-hydroxyethyl)-2,5-diaminobenzene, N,N-bis-(2-hydroxyethyl)-p-phenylenediamine, 2-(2,5-diaminophenoxy)-ethanol, 1-phenyl-3-carboxyamido-4-amino-5-pyrazolone, 4-amino-3-methylphenol, 2,4,5,6-tetraaminopyrimidine, 2-hydroxy-4,5,6-tri-aminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-  
30 diaminopyrimidine, 2-dimethylamino-4,5,6-triaminopyrimidine, 2-hydroxy-

ethylaminomethyl-4-aminophenol, 4,4'-diaminodiphenylamine, 4-amino-3-fluorophenol, 2-aminomethyl-4-aminophenol, 2-hydroxymethyl-4-aminophenol, bis-(2-hydroxy-5-aminophenyl)-methane, 1,4-bis-(4-aminophenyl)-diazacycloheptane, 1,3-bis-(N-(2-hydroxyethyl)-N-(4-aminophenylamino))-2-propanol, 4-amino-2-(2-hydroxyethoxy)-phenol and 4,5-diaminopyrazole derivatives according to **EP 0 740 741** or **WO 94/08970**, for example 4,5-diamino-1-(2'-hydroxyethyl)-pyrazole. Particularly preferred primary intermediates are p-phenylenediamine, p-toluylenediamine, p-aminophenol, 1-(2'-hydroxyethyl)-2,5-diaminobenzene, 4-amino-3-methylphenol, 2-aminomethyl-4-aminophenol, 2,4,5,6-tetraaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine and 4-hydroxy-2,5,6-triaminopyrimidine.

m-Phenylenediamine derivatives, naphthols, resorcinol and resorcinol derivatives, pyrazolones and m-aminophenol derivatives are generally used as oxidation dye precursors of the secondary intermediate type. According to the invention, preferred secondary intermediates are 1-naphthol, pyrogallol, 1,5-, 2,7- and 1,7-dihydroxynaphthalene, o-aminophenol, 5-amino-2-methylphenol, m-aminophenol, resorcinol, resorcinol monomethyl ether, m-phenylenediamine, 1-phenyl-3-methyl-5-pyrazolone, 2,4-dichloro-3-aminophenol, 1,3-bis-(2,4-diaminophenoxy)-propane, 4-chlororesorcinol, 2-chloro-6-methyl-3-aminophenol, 2-methyl resorcinol, 5-methyl resorcinol, 2,5-dimethyl resorcinol, 2,6-dihydroxypyridine, 2,6-diaminopyridine, 2-amino-3-hydroxypyridine, 2,6-dihydroxy-3,4-diaminopyridine, 3-amino-2-methylamino-6-methoxypyridine, 4-amino-2-hydroxytoluene, 2,6-bis-(2-hydroxyethylamino)-toluene, 2,4-diaminophenoxyethanol, 1-methoxy-2-amino-4-(2-hydroxyethylamino)-benzene, 2-methyl-4-chloro-5-aminophenol, 6-methyl-1,2,3,4-tetrahydroquinoxaline, 3,4-methylenedioxyphenol, 3,4-methylenedioxyaniline, 2,6-dimethyl-3-aminophenol, 3-amino-6-methoxy-2-methylaminophenol, 2-hydroxy-4-aminophenoxy ethanol, 2-methyl-5-(2-hydroxyethylamino)-phenol and 2,6-dihydroxy-3,4-dimethyl pyridine. Particularly preferred secondary

intermediates are 1-naphthol, 1,5-, 2,7- and 1,7-dihydroxynaphthalene, 5-amino-2-methylphenol, resorcinol, 4-chlororesorcinol, 2-chloro-6-methyl-3-aminophenol, 2-methyl resorcinol, 5-methyl resorcinol, 2,5-dimethyl resorcinol and 2,6-dihydroxy-3,4-diaminopyridine.

5           Substantive dyes are normally nitrophenylenediamines, nitro-aminophenols, azo dyes, anthraquinones or indophenols. Preferred substantive dyes are the compounds known under the International names or trade names of HC Yellow 2, HC Yellow 4, HC Yellow 5, HC Yellow 6, Basic Yellow 57, Disperse Orange 3, HC Red 3, HC Red BN, Basic Red  
10 76, HC Blue 2, HC Blue 12, Disperse Blue 3, Basic Blue 99, HC Violet 1, Disperse Violet 1, Disperse Violet 4, Disperse Black 9, Basic Brown 16 and Basic Brown 17 and also 1,4-bis-( $\beta$ -hydroxyethyl)-amino-2-nitrobenzene, 4-amino-2-nitrodiphenylamine-2'-carboxylic acid, 6-nitro-1,2,3,4-tetrahydro-  
15 quinoxaline, hydroxyethyl-2-nitrotoluidine, picramic acid, 2-amino-6-chloro-4-nitrophenol, 4-ethylamino-3-nitrobenzoic acid and 2-chloro-6-ethylamino-1-hydroxy-4-nitrobenzene.

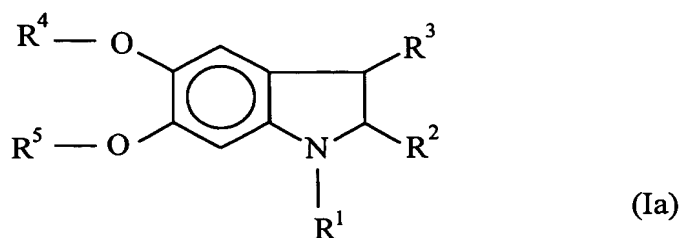
          The preparations according to the invention may also contain naturally occurring dyes such as, for example, henna red, henna neutral, henna black, camomile blossom, sandalwood, black tea, black alder bark,  
20 sage, logwood, madder root, catechu, sedre and alkanet.

          Both the oxidation dye precursors and the substantive dyes are present in the preparations according to the invention in quantities of preferably 0.01 to 20% by weight and more preferably 0.5 to 5% by weight, based on the preparation as a whole.

25           Preferred precursors of natural dyes are indoles and indolines which contain at least one hydroxy or amino group, preferably as a substituent on the six-membered ring. These groups may carry further substituents, for example in the form of an etherification or esterification of the hydroxy group or an alkylation of the amino group.

30           Particularly suitable precursors of natural hair dyes are derivatives of

5,6-dihydroxyindoline corresponding to formula (IIa):



10 in which - independently of one another -  $R^1$  is hydrogen, a  $C_{1-4}$  alkyl group or a  $C_{1-4}$  hydroxyalkyl group,

$R^2$  is hydrogen or a  $-COOH$  group, the  $-COOH$  group optionally being present as a salt with a physiologically compatible cation,

15  $R^3$  is hydrogen or a  $C_{1-4}$  alkyl group,

$R^4$  is hydrogen, a  $C_{1-4}$  alkyl group or a group  $-CO-R^6$ , where  $R^6$  is a  $C_{1-4}$  alkyl group, and

$R^5$  is one of the groups mentioned for  $R^4$ ,

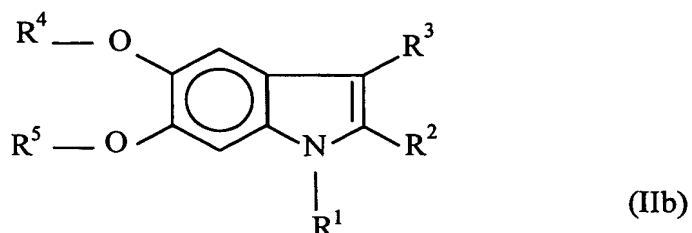
20 and physiologically compatible salts of these compounds with an organic or inorganic acid.

Particularly preferred derivatives of indoline are 5,6-dihydroxyindoline, N-methyl-5,6-dihydroxyindoline, N-ethyl-5,6-dihydroxyindoline, N-propyl-5,6-dihydroxyindoline, N-butyl-5,6-dihydroxyindoline, 5,6-dihydroxyindoline-2-carboxylic acid and 6-hydroxyindoline, 6-aminoindoline and 4-aminoindoline.

25 Within this group, particular emphasis is placed on N-methyl-5,6-dihydroxyindoline, N-ethyl-5,6-dihydroxyindoline, N-propyl-5,6-dihydroxyindoline, N-butyl-5,6-dihydroxyindoline and, in particular, 5,6-dihydroxyindoline.

30 Other particularly suitable precursors of natural hair dyes are derivatives of 5,6-dihydroxyindole corresponding to formula (IIb):

5



in which - independently of one another -

- 10  $R^1$  is hydrogen, a  $C_{1-4}$  alkyl group or a  $C_{1-4}$  hydroxyalkyl group,  
 $R^2$  is hydrogen or a  $-COOH$  group, the  $-COOH$  group optionally being present as a salt with a physiologically compatible cation,  
 $R^3$  is hydrogen or a  $C_{1-4}$  alkyl group,  
 $R^4$  is hydrogen, a  $C_{1-4}$  alkyl group or a group  $-CO-R^6$ , where  $R^6$  is a  $C_{1-4}$   
 15 alkyl group, and  
 $R^5$  is one of the groups mentioned for  $R^4$ ,  
 or physiologically compatible salts of these compounds with an organic or inorganic acid.

Particularly preferred derivatives of indole are 5,6-dihydroxyindole,  
 20 N-methyl-5,6-dihydroxyindole, N-ethyl-5,6-dihydroxyindole, N-propyl-5,6-dihydroxyindole, N-butyl-5,6-dihydroxyindole, 5,6-dihydroxyindole-2-carboxylic acid, 6-hydroxyindole, 6-aminoindole and 4-aminoindole.

Within this group, particular emphasis is placed on N-methyl-5,6-dihydroxyindole, N-ethyl-5,6-dihydroxyindole, N-propyl-5,6-dihydroxyindole,  
 25 N-butyl-5,6-dihydroxyindole and, in particular, 5,6-dihydroxyindole.

The indoline and indole derivatives may be used both as free bases and in the form of their physiologically compatible salts with inorganic or organic acids, for example hydrochlorides, sulfates and hydrobromides, in the colorants used in the process according to the invention. The indole or  
 30 indoline derivatives are present in these colorants in quantities of normally 0.05 to 10% by weight and preferably 0.2 to 5% by weight.



Where dye precursors of the indoline or indole type are used, it can be of advantage to use them together with at least one amino acid and/or at least one oligopeptide. Preferred amino acids are aminocarboxylic acids, more particularly  $\alpha$ -aminocarboxylic acids and  $\omega$ -aminocarboxylic acids. Among the  $\alpha$ -aminocarboxylic acids, arginine, lysine, ornithine and histidine are particularly preferred. A most particularly preferred amino acid is arginine used more particularly in free form but also as the hydrochloride. The corresponding preparations contain the amino acid or the oligopeptide in quantities of 0.1 to 10% by weight and preferably 1 to 4% by weight, based on the preparation as a whole.

The oxidation dye precursors, the substantive dyes or the precursors of natural dyes do not have to be single compounds. On the contrary, other components may be present in small quantities in the hair colorants according to the invention due to the processes used to produce the individual dyes providing these other components do not adversely affect the coloring result or have to be ruled out for other reasons, for example toxicological reasons.

So far as the dyes suitable for use in the hair colorants and tinting compositions according to the invention are concerned, reference is also expressly made to the work by Ch. Zviak, **The Science of Hair Care, Chapter 7** (pages 248-250; substantive dyes) and **Chapter 8**, pages 264-267; oxidation dye precursors), published as Volume 7 of the Series **"Dermatology"** (Ed.: Ch. Culnan and H. Maibach), Marcel Dekker Inc., New York/Basel, 1986, and to the **"Europäische Inventar der Kosmetik-Rohstoffe"** published by the Europäische Gemeinschaft and available in disk form from the Bundesverband Deutscher Industrie- und Handelsunternehmen für Arzneimittel, Reformwaren und Körperpflegemittel d.V., Mannheim.

To produce the colorants, the compulsory and optional constituents mentioned above are incorporated in a suitable water-containing carrier.

For coloring hair, such carriers are, for example, creams, emulsions, gels or even surfactant-containing foaming solutions, for example shampoos, foam aerosols or other formulations suitable for application to the hair.

Hair colorants are normally adjusted to a mildly acidic to alkaline pH, i.e. to a pH of about 5 to 11, particularly where coloring is carried out oxidatively with atmospheric oxygen or other oxidizing agents, such as hydrogen peroxide. To this end, the colorants contain alkalizing agents, normally alkali metal or alkaline earth metal hydroxides, ammonia or organic amines. Preferred alkalizing agents are monoethanolamine, monoisopropanolamine, 2-amino-2-methylpropanol, 2-amino-2-methylpropane-1,3-diol, 2-amino-2-ethylpropane-1,3-diol, 2-amino-2-methylbutanol and triethanolamine and alkali metal and alkaline earth metal hydroxides. Within this group, monoethanolamine, triethanolamine and 2-amino-2-methylpropanol and 2-amino-2-methylpropane-1,3-diol are preferred.  $\omega$ -Amino acids, such as  $\omega$ -aminocaproic acid, may also be used as alkalizing agents.

The colorants according to the invention may also contain any of the known active substances, additives and auxiliaries typical of such formulations. In many cases, the colorants contain at least one surfactant, both anionic and zwitterionic, ampholytic, nonionic and cationic surfactants being suitable in principle. In many cases, however, it has been found to be of advantage to select the surfactants from anionic, zwitterionic or nonionic surfactants. Anionic surfactants can be particularly useful.

So far as the anionic and cationic surfactants are concerned, reference is made to the foregoing observations.

In the context of the invention, zwitterionic surfactants are surface-active compounds which contain at least one quaternary ammonium group and at least one  $-\text{COO}^{(-)}$  or  $-\text{SO}_3^{(-)}$  group in the molecule. Particularly suitable zwitterionic surfactants are the so-called betaines, such as N-alkyl-N,N-dimethyl ammonium glycinate, for example cocoalkyl dimethyl

ammonium glycinate, N-acylaminopropyl-N,N-dimethyl ammonium glycinate, for example cocoacylaminopropyl dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl imidazolines containing 8 to 18 carbon atoms in the alkyl or acyl group and  
5 cocoacylaminoethyl hydroxyethyl carboxymethyl glycinate. A preferred zwitterionic surfactant is the fatty acid amide derivative known by the CTFA name of Cocamidopropyl Betaine.

Ampholytic surfactants are surface-active compounds which, in addition to a C<sub>8-18</sub> alkyl or acyl group, contain at least one free amino group and at least one -COOH or -SO<sub>3</sub>H group in the molecule and which are  
10 capable of forming inner salts. Examples of suitable ampholytic surfactants are N-alkyl glycines, N-alkyl propionic acids, N-alkyl aminobutyric acids, N-alkyl iminodipropionic acids, N-hydroxyethyl-N-alkyl amidopropyl glycines, N-alkyl taurines, N-alkyl sarcosines, 2-alkyl aminopropionic acids and alkyl  
15 aminoacetic acids containing around 8 to 18 carbon atoms in the alkyl group. Particularly preferred ampholytic surfactants are N-cocoalkyl amino-propionate, cocoacyl aminoethyl aminopropionate and C<sub>12-18</sub> acyl sarcosine.

Nonionic surfactants contain, for example, a polyol group, a poly-  
20 alkylene glycol ether group or a combination of polyol and polyglycol ether groups as the hydrophilic group. Examples of such compounds are

- products of the addition of 2 to 30 moles of ethylene oxide and/or 0 to 5 moles of propylene oxide to linear fatty alcohols containing 8 to 22 carbon atoms, to fatty acids containing 12 to 22 carbon atoms and to  
25 alkylphenols containing 8 to 15 carbon atoms in the alkyl group,
- C<sub>12-22</sub> fatty acid monoesters and diesters of products of the addition of 1 to 30 moles of ethylene oxide to glycerol,
- C<sub>8-22</sub> alkyl mono- and oligoglycosides and ethoxylated analogs thereof,
- products of the addition of 5 to 60 moles of ethylene oxide to castor oil  
30 and hydrogenated castor oil,

- products of the addition of ethylene oxide to sorbitan fatty acid esters,
- products of the addition of ethylene oxide to fatty acid alkanolamides.

5       The compounds containing alkyl groups used as surfactants may be single compounds. In general, however, these compounds are produced from native vegetable or animal raw materials so that mixtures with different alkyl chain lengths dependent upon the particular raw material are obtained.

10       The surfactants representing addition products of ethylene and/or propylene oxide with fatty alcohols or derivatives of these addition products may be both products with a "normal" homolog distribution and products with a narrow homolog distribution. Products with a "normal" homolog distribution are mixtures of homologs which are obtained in the reaction of fatty alcohol and alkylene oxide using alkali metals, alkali metal hydroxides  
15       or alkali metal alcoholates as catalysts. By contrast, narrow homolog distributions are obtained when, for example, hydrotalcites, alkaline earth metal salts of ether carboxylic acids, alkaline earth metal oxides, hydroxides or alcoholates are used as catalysts. The use of products with a narrow homolog distribution can be of advantage.

20       Other active substances, auxiliaries and additives are, for example,  
- nonionic polymers such as, for example, vinyl pyrrolidone/vinyl acrylate copolymers, polyvinyl pyrrolidone and vinyl pyrrolidone/vinyl acetate copolymers and polysiloxanes,  
- cationic polymers, such as quaternized cellulose ethers, polysiloxanes  
25       containing quaternary groups, dimethyl diallyl ammonium chloride polymers, acrylamide/dimethyl diallyl ammonium chloride copolymers, dimethyl aminoethyl methacrylate/vinyl pyrrolidone copolymers quaternized with diethyl sulfate, vinyl pyrrolidone/imidazolium methochloride copolymers and quaternized polyvinyl alcohol,  
30       - zwitterionic and amphoteric polymers such as, for example, acrylamido-

propyl/trimethyl ammonium chloride/acrylate copolymers and octyl acrylamide/methyl methacrylate/tert.butyl aminoethyl methacrylate/2-hydroxypropyl methacrylate copolymers,

- 5 - anionic polymers such as, for example, polyacrylic acids, crosslinked polyacrylic acids, vinyl acetate/crotonic acid copolymers, vinyl pyrrolidone/vinyl acrylate copolymers, vinyl acetate/butyl maleate/isobornyl acrylate copolymers, methyl vinyl ether/maleic anhydride copolymers and acrylic acid/ethyl acrylate/N-tert.butyl acrylamide terpolymers,
- 10 - thickeners, such as agar agar, guar gum, alginates, xanthan gum, gum arabic, karaya gum, locust bean gum, linseed gums, dextrans, cellulose derivatives, for example methyl cellulose, hydroxyalkyl cellulose and carboxymethyl cellulose, starch fractions and derivatives, such as amylose, amylopectin and dextrans, clays such as, for example,
- 15 bentonite or fully synthetic hydrocolloids such as, for example, polyvinyl alcohol,
- structurants, such as maleic acid and lactic acid,
- hair-conditioning compounds, such as phospholipids, for example soybean lecithin, egg lecithin and kephalins, and also silicone oils,
- 20 - protein hydrolyzates, more particularly elastin, collagen, keratin, milk protein, soybean protein and wheat protein hydrolyzates, condensation products thereof with fatty acids and quaternized protein hydrolyzates,
- perfume oils, dimethyl isosorbide and cyclodextrins,
- solvents and solubilizers, such as ethanol, isopropanol, ethylene glycol,
- 25 propylene glycol, glycerol and diethylene glycol,
- antidandruff agents, such as Piroctone Olamine and Zinc Omadine,
- other substances for adjusting the pH value, such as for example  $\alpha$ - and  $\beta$ -hydroxycarboxylic acids,
- active principles, such as panthenol, pantothenic acid, allantoin,
- 30 pyrrolidone carboxylic acids and salts thereof, plant extracts and

- vitamins,
- cholesterol,
  - consistency factors, such as sugar esters, polyol esters or polyol alkyl ethers,
  - 5 - fats and waxes, such as spermaceti, beeswax and montan wax,
  - fatty acid alkanolamides,
  - complexing agents, such as EDTA, NTA and phosphonic acids,
  - swelling and penetration agents, such as glycerol, propylene glycol monoethyl ether, carbonates, hydrogen carbonates, guanidines, ureas
  - 10 and primary, secondary and tertiary phosphates,
  - opacifiers, such as latex,
  - pearlizers, such as ethylene glycol mono- and distearate,
  - propellents, such as propane/butane mixtures, N<sub>2</sub>O, dimethyl ether, CO<sub>2</sub> and air and
  - 15 - antioxidants.

To produce the colorants according to the invention, the constituents of the water-containing carrier are used in the usual quantities for this purpose. For example, emulsifiers are used in concentrations of 0.5 to

20 30% by weight while thickeners are used in concentrations of 0.1 to 25% by weight, based on the colorant as a whole.

Information on other optional components and the quantities in which they are used can be found in the reference books known to the expert, for example K. Schrader, **Grundlagen und Rezepturen der**

25 **Kosmetika, 2nd Edition, Hüthig Buch Verlag, Heidelberg, 1989.**

If the actual hair colors are developed in an oxidative process, typical oxidizing agents such as, in particular, hydrogen peroxide or adducts thereof with urea, melamine or sodium borate may be used. However, oxidation with atmospheric oxygen as sole oxidizing agent may

30 be preferred. Oxidation may also be carried out with enzymes. In this

case, the enzymes may be used both to produce oxidizing per compounds and to enhance the effect of an oxidizing agent present in small quantities. Examples of enzymatic processes include the use of laccases and strengthening of the effect of small quantities (for example 1% and less, 5 based on the formulation as a whole) of hydrogen peroxide by peroxidases.

The preparation of the oxidizing agent is preferably mixed with the preparation of the oxidation dye precursors immediately before coloring of the hair. The ready-to-use hair coloring preparation formed should have a pH value in the range from 6 to 10. In a particularly preferred embodiment, 10 the hair colorant is used in a mildly alkaline medium. The application temperatures may be in the range from 15 to 40°C but are preferably at the temperature of the scalp. After a contact time of about 5 to 45 and preferably 15 to 30 minutes, the hair colorant is removed from the hair to be colored by rinsing. There is no need for the hair to be washed with a 15 shampoo where a carrier of high surfactant content, for example a coloring shampoo, has been used.

In the particular case of hair which is difficult to color, the preparation containing the oxidation dye precursors may be applied to the hair without preliminary mixing with the oxidation component. The oxidation component 20 is applied after a contact time of 20 to 30 minutes, optionally after rinsing. After another contact time of 10 to 20 minutes, the hair is rinsed and, if desired, shampooed. In a first variant of this embodiment where the preliminary application of the dye precursors is intended to improve penetration into the hair, the corresponding formulation is adjusted to a pH 25 value of about 4 to 7. In a second variant, oxidation with air is initially carried out, the formulation applied preferably having a pH value of 7 to 10. In the subsequent accelerated post-oxidation phase, it can be of advantage to use acidified peroxydisulfate solutions as the oxidizing agent.

30 Whichever of the processes mentioned above is used to apply the colorant according to the invention, development of the color may be

supported and enhanced by adding certain metal ions to the colorant. Examples of such metal ions are  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mn}^{4+}$ ,  $\text{Li}^{+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$ .  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  are particularly suitable. Basically, the metal ions may be used in the form of a physiologically compatible salt. Preferred salts are the acetates, sulfates, halides, lactates and tartrates. Development of the hair color can be accelerated and the color tone can be influenced as required through the use of these metal salts.

As mentioned above, application of the UV filter to increase the fastness of the colors of keratin fibers to washing may also be carried out in a separate step after the actual coloring step.

Accordingly, the present invention also relates to a process for coloring keratin fibers, characterized in that, in a first step, the keratin fiber is colored in the usual way and, in a second step, a preparation containing at least one UV filter to increase the fastness of the color to washing is applied and, if desired, is rinsed out again after a contact time of a few seconds to about 20 minutes.

In the context of the invention, the expression "colored in the usual way" is understood to mean the procedure known to the expert whereby a colorant is applied to the - optionally wetted - hair and is left on the hair for a time of a few minutes to about 45 minutes. The hair is then rinsed out with water or a surfactant-containing preparation.

The second step of the process according to the invention, in which the preparation containing the UV filter is applied, can be:

- The above-mentioned rinsing out of the colorant, the water or the surfactant preparation additionally containing a UV filter.
- The application of another preparation containing a UV filter after the rinsing step mentioned, this other preparation also being removed from the hair after a contact time of a few seconds to about 20 minutes. In this case, the other preparation may be, for example, a



hair treatment preparation of the rinse or conditioner type.

- The application of another preparation containing a UV filter after the rinsing step mentioned, this other preparation remaining on the hair. In this case, the other preparation may be, for example, a hair treatment preparation such as a conditioner, an aftertreatment or a hair spray.

This second preparation which is used to apply the UV filter to the hair may contain the other ingredients typical of the type of preparation selected. Reference is specifically made in this connection both to the basic knowledge of the relevant expert, as documented for example by Schrader's work cited above, and to the other ingredients listed above in the description of the colorants. In principle, the way in which this second preparation is made up is not subject to any restrictions either. Creams, lotions, solutions, emulsions, gels, sprays and surfactant-containing foaming solutions, for example shampoos or foam aerosols, are suitable. However, formulation as a so-called PIT emulsion can be less preferred on account of the associated limitations in regard to the other ingredients.

Finally, a particularly marked improvement in the fastness to washing of colors on keratin fibers was observed when a preparation containing a combination of a water-insoluble UV filter, a UV filter corresponding to formula (I) and a mono-, di- or oligosaccharide was used.

Accordingly, the present invention also relates to a preparation for increasing the fastness to washing of colors on keratin fibers, characterized in that it contains an active-principle combination consisting of at least one water-insoluble UV filter, an least one UV filter corresponding to formula (I) and a mono-, di- or oligosaccharide.

According to the foregoing, this preparation may be both the actual colorant and a preparation which is applied to the hair in a second step after the actual coloring step. With regard to the preferred embodiments as

to the compulsory ingredients and the other optional components of these preparations according to the invention, reference is made to the foregoing observations.

The following Examples are intended to illustrate the invention.

5

### Examples

All quantities in the following Examples are parts by weight unless otherwise indicated.

10 Colorant formulation

Oleic acid	6.5
Propylene glycol	6.5
Isopropanol	12.0
Sodium lauryl ether sulfate + 2 EO	3.5

15 (27% active substance in water)

Sodium sulfite	0.2
EDTA disodium salt	0.1
p-Aminophenol HCl	0.5
p-Toluylenediamine sulfate	0.1

20 Resorcinol

4-Amino-2-nitrodiphenylamine-2'-carboxylic acid	0.1
6-Nitro-1,2,3,4-tetrahydroquinoxaline	0.1
5-Amino-2-methylphenol	0.3
Perfume	0.5

25 Monoethanolamine

to pH 9.2

Water

to 100

30 The colorant was mixed with a commercially available primary intermediate (Poly Country Colors) containing 5% hydrogen peroxide in a ratio of colorant to primary intermediate of 40 ml to 50 ml.

## Conditioner formulations

	B1	B2	C1
C <sub>16/18</sub> fatty alcohol (1:1)	3.0	3.0	3.0
5 Paraffin oil perliq.	3.0	3.0	3.0
Cetyl trimethyl ammonium chloride	0.8	0.8	0.8
Perfume	0.3	0.3	0.3
Escalol® HP610 <sup>1</sup>	1.0	-	-
Uvinul® M 40 <sup>2</sup>	-	0.5	-
10 Water	←----- to 100 -----→		

<sup>1</sup> dodecyl dimethylaminobenzamidopropyl dimethyl ammonium tosylate (ISP)

<sup>2</sup> 2-hydroxy-4-methoxybenzophenone (INCI name: Benzophenone-3)  
15 (BASF)

Coloring was carried out on natural white hair tresses (ca. 2 g) of the Virgin White (Alkinco) type. To this end, 8 g of the colorant/primary intermediate mixture were applied to the tress, left thereof for 30 mins. and  
20 then rinsed out with water (37°C). The tress was then treated for 2 mins. with the conditioner (B1, B2 and C1), then washed 6 times with 0.5 ml of a commercially available shampoo, rinsed with water (37°C) and dried.

The color intensity of the tress was then evaluated by experts using the following scoring system:  
25 color intensity = 1: Virgin White tress before coloring  
color intensity = 6: tress after coloring, rinsing with water (37°C) and drying (no treatment with the conditioner)

The following scores were awarded:

Conditioner	Score
B1	5
B2	5
V1	4

5

Accordingly, the fastness of the colors to washing was significantly higher on the tresses aftertreated in accordance with the invention than on the tresses aftertreated with the comparison preparation.

**CLAIMS**

1. The use of a UV filter for improving the fastness to washing of colors on keratin fibers.
2. The use claimed in claim 1, characterized in that the UV filter is insoluble in water.
3. The use claimed in claim 1 or 2, characterized in that the UV filter contains a benzophenone unit.
4. The use claimed in claim 1, characterized in that the UV filter contains a cationic group.
5. The use claimed in claim 4, characterized in that the UV filter has a general structure corresponding to formula (I):

U - Q

(I)

- in which U is a UV-absorbing group and Q is a group containing at least one quaternary ammonium function.
6. The use claimed in claim 5, characterized in that the group Q in general formula (I) has the general structure  $-(CH_2)_x N^+ R^1 R^2 R^3 X^-$ , where x is an integer of 1 to 4,  $R^1$  and  $R^2$  independently of one another represent  $C_{1-4}$  alkyl groups,  $R^3$  is a  $C_{1-22}$  alkyl group or a benzyl group and  $X^-$  is a physiologically compatible anionic group.
7. The use claimed in claim 6, characterized in that at least two of the groups  $R^1$ ,  $R^2$  and  $R^3$  are methyl groups.
8. The use claimed in any of claims 5 to 7, characterized in that the group U is selected so that the UV filter A has an absorption maximum in the UVB range.
9. The use claimed in any of claims 1 to 8, characterized in that the UV filter has a molar extinction coefficient at the absorption maximum of at least 15,000.
10. The use claimed in at least one of claims 1 to 9, characterized in that

the UV filter is used in combination with a mono-, di- or oligosaccharide.

11. The use claimed in any of claims 1 to 10, characterized in that the UV filter is used in combination with a spreading agent.

5 12. The use claimed in claim 11, characterized in that the spreading agent is paraffin oil.

13. A process for coloring keratin fibers, characterized in that, in a first step, the keratin fiber is colored in the usual way and, in a second step, a preparation containing at least one UV filter to increase the fastness of the color to washing is applied and, if desired, is rinsed out again after a  
10 contact time of a few seconds to about 20 minutes.

14. A process for coloring keratin fibers in the usual way with a colorant, characterized in that the colorant contains a UV filter to increase the fastness of the color to washing.

15 15. A composition for increasing the fastness to washing of colors on keratin fibers, characterized in that it contains a combination of active substances consisting of

- at least one water-insoluble UV filter
- at least one UV filter corresponding to formula (I) in claim 5 and
- a mono-, di- or oligosaccharide.

**Translation**

PATENT COOPERATION TREATY

**PCT**

**INTERNATIONAL PRELIMINARY EXAMINATION REPORT**

(PCT Article 36 and Rule 70)

3

Applicant's or agent's file reference H 3609 PCT		<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/EP00/08923	International filing date ( <i>day/month/year</i> ) 13 September 2000 (13.09.00)	Priority date ( <i>day/month/year</i> ) 22 September 1999 (22.09.99)	
International Patent Classification (IPC) or national classification and IPC A61K 7/13			
Applicant HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN			

<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of <u>5</u> sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of _____ sheets.</p>	
<p>3. This report contains indications relating to the following items:</p> <p>I <input checked="" type="checkbox"/> Basis of the report</p> <p>II <input type="checkbox"/> Priority</p> <p>III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p>IV <input type="checkbox"/> Lack of unity of invention</p> <p>V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p>VI <input checked="" type="checkbox"/> Certain documents cited</p> <p>VII <input type="checkbox"/> Certain defects in the international application</p> <p>VIII <input type="checkbox"/> Certain observations on the international application</p>	

Date of submission of the demand 05 April 2001 (05.04.01)	Date of completion of this report 19 October 2001 (19.10.2001)
Name and mailing address of the IPEA/EP	Authorized officer
Facsimile No.	Telephone No.

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/EP00/08923

## I. Basis of the report

1. This report has been drawn on the basis of *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.)*:

- ☐ the international application as originally filed.
- ☒ the description, pages 1-38, as originally filed,  
 pages \_\_\_\_\_, filed with the demand,  
 pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_,  
 pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_.
- ☒ the claims, Nos. 1-17, as originally filed,  
 Nos. \_\_\_\_\_, as amended under Article 19,  
 Nos. \_\_\_\_\_, filed with the demand,  
 Nos. \_\_\_\_\_, filed with the letter of \_\_\_\_\_,  
 Nos. \_\_\_\_\_, filed with the letter of \_\_\_\_\_.
- ☐ the drawings, sheets/fig \_\_\_\_\_, as originally filed,  
 sheets/fig \_\_\_\_\_, filed with the demand,  
 sheets/fig \_\_\_\_\_, filed with the letter of \_\_\_\_\_,  
 sheets/fig \_\_\_\_\_, filed with the letter of \_\_\_\_\_.

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages \_\_\_\_\_
- ☐ the claims, Nos. \_\_\_\_\_
- ☐ the drawings, sheets/fig \_\_\_\_\_

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

4. Additional observations, if necessary:



## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/EP 00/08923

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

## 1. Statement

Novelty (N)	Claims	3-17	YES
	Claims	1, 2	NO
Inventive step (IS)	Claims	3-17	YES
	Claims		NO
Industrial applicability (IA)	Claims	1-17	YES
	Claims		NO

## 2. Citations and explanations

Reference is made to the following documents cited in the international search report:

D1: US-A-5 490 980

D2: GARDENER, JOHN M. ET AL.: 'An investigation into the action of transglutaminase on human hair' J. SOC. COSMET. CHEM., Vol. 46, No. 1, February 1995 (1995-02), pages 11-28.

*Novelty (PCT Article 33(2))*

1. D1 describes a method for applying an active component to human hair, wherein a composition is used which, in addition to transglutaminase, contains an active substance which has a substrate activity for this enzyme (cf. Claims 6 and 1). This active substance is selected from a group which includes dyes (cf. Claim 3; col. 7, line 64 to col. 8, line 18).

D1 therefore discloses a method which is covered by the broad wording of independent Claim 1 and dependent Claim 2. These claims cannot therefore be considered novel.

2. The additional features of dependent Claims 3-13 in combination with independent Claim 1 are not disclosed in any of the international search report citations. They therefore meet the PCT novelty requirements.
3. The subjects of the additional independent Claims 14-17 are not disclosed in the international search report citations either and are therefore likewise considered novel.

*Inventive step (PCT Article 33(3))*

1. In D1, active components are bonded to human skin, hair and nails using the enzyme transglutaminase.

D2 examines the behaviour of transglutaminase on human hair; for example, with proteins, transglutaminase forms a cross-linked layer which covers and protects the hair.

2. However, none of the documents mentions or suggests that the application of transglutaminase together with a substrate-active substance (e.g. proteins) improves the wash resistance of dyed keratin fibres, in particular hair.

The subject matter of independent Claims 14-17 and of dependent Claims 3-13 therefore involves an inventive step.

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/EP00/08923

## VI. Certain documents cited

### 1. Certain published documents (Rule 70.10)

Application No. Patent No.	Publication date (day/month/year)	Filing date (day/month/year)	Priority date (valid claim) (day/month/year)
-------------------------------	--------------------------------------	---------------------------------	---

### 2. Non-written disclosures (Rule 70.9)

Kind of non-written disclosure	Date of non-written disclosure (day/month/year)	Date of written disclosure referring to non-written disclosure (day/month/year)
--------------------------------	--	---

See annex

# VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS

## PCT

REC'D 23 OCT 2001

## INTERNATIONALER VORLÄUFIGER PRÜFUNGSBERICHT

(Artikel 36 und Regel 70 PCT)

Aktenzeichen des Anmelders oder Anwalts H 3609 PCT	<b>WEITERES VORGEHEN</b> siehe Mitteilung über die Übersendung des internationalen vorläufigen Prüfungsberichts (Formblatt PCT/IPEA/416)	
Internationales Aktenzeichen PCT/EP00/08923	Internationales Anmeldedatum (Tag/Monat/Jahr) 13/09/2000	Prioritätsdatum (Tag/Monat/Jahr) 22/09/1999
Internationale Patentklassifikation (IPK) oder nationale Klassifikation und IPK A61K7/13		
Anmelder HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN et al.		


- Dieser internationale vorläufige Prüfungsbericht wurde von der mit der internationalen vorläufigen Prüfung beauftragten Behörde erstellt und wird dem Anmelder gemäß Artikel 36 übermittelt.
- Dieser BERICHT umfaßt insgesamt 5 Blätter einschließlich dieses Deckblatts.
 

☐ Außerdem liegen dem Bericht ANLAGEN bei; dabei handelt es sich um Blätter mit Beschreibungen, Ansprüchen und/oder Zeichnungen, die geändert wurden und diesem Bericht zugrunde liegen, und/oder Blätter mit vor dieser Behörde vorgenommenen Berichtigungen (siehe Regel 70.16 und Abschnitt 607 der Verwaltungsrichtlinien zum PCT).

Diese Anlagen umfassen insgesamt Blätter.

3. Dieser Bericht enthält Angaben zu folgenden Punkten:

- I ☒ Grundlage des Berichts
- II ☐ Priorität
- III ☐ Keine Erstellung eines Gutachtens über Neuheit, erfinderische Tätigkeit und gewerbliche Anwendbarkeit
- IV ☐ Mangelnde Einheitlichkeit der Erfindung
- V ☒ Begründete Feststellung nach Artikel 35(2) hinsichtlich der Neuheit, der erfinderischen Tätigkeit und der gewerblichen Anwendbarkeit; Unterlagen und Erklärungen zur Stützung dieser Feststellung
- VI ☒ Bestimmte angeführte Unterlagen
- VII ☐ Bestimmte Mängel der internationalen Anmeldung
- VIII ☐ Bestimmte Bemerkungen zur internationalen Anmeldung

Datum der Einreichung des Antrags  05/04/2001	Datum der Fertigstellung dieses Berichts  19.10.2001
Name und Postanschrift der mit der internationalen vorläufigen Prüfung beauftragten Behörde:   Europäisches Patentamt D-80298 München Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Bevollmächtigter Bediensteter  Renoth, H  Tel. Nr. +49 89 2399 8589



**I. Grundlage des Berichts**

1. Hinsichtlich der **Bestandteile** der internationalen Anmeldung (*Ersatzblätter, die dem Anmeldeamt auf eine Aufforderung nach Artikel 14 hin vorgelegt wurden, gelten im Rahmen dieses Berichts als "ursprünglich eingereicht" und sind ihm nicht beigefügt, weil sie keine Änderungen enthalten (Regeln 70.16 und 70.17)*):  
**Beschreibung, Seiten:**

1-38                      ursprüngliche Fassung

**Patentansprüche, Nr.:**

1-17                      ursprüngliche Fassung

2. Hinsichtlich der **Sprache**: Alle vorstehend genannten Bestandteile standen der Behörde in der Sprache, in der die internationale Anmeldung eingereicht worden ist, zur Verfügung oder wurden in dieser eingereicht, sofern unter diesem Punkt nichts anderes angegeben ist.

Die Bestandteile standen der Behörde in der Sprache: zur Verfügung bzw. wurden in dieser Sprache eingereicht; dabei handelt es sich um

- ☐ die Sprache der Übersetzung, die für die Zwecke der internationalen Recherche eingereicht worden ist (nach Regel 23.1(b)).
- ☐ die Veröffentlichungssprache der internationalen Anmeldung (nach Regel 48.3(b)).
- ☐ die Sprache der Übersetzung, die für die Zwecke der internationalen vorläufigen Prüfung eingereicht worden ist (nach Regel 55.2 und/oder 55.3).

3. Hinsichtlich der in der internationalen Anmeldung offenbarten **Nucleotid- und/oder Aminosäuresequenz** ist die internationale vorläufige Prüfung auf der Grundlage des Sequenzprotokolls durchgeführt worden, das:

- ☐ in der internationalen Anmeldung in schriftlicher Form enthalten ist.
- ☐ zusammen mit der internationalen Anmeldung in computerlesbarer Form eingereicht worden ist.
- ☐ bei der Behörde nachträglich in schriftlicher Form eingereicht worden ist.
- ☐ bei der Behörde nachträglich in computerlesbarer Form eingereicht worden ist.
- ☐ Die Erklärung, daß das nachträglich eingereichte schriftliche Sequenzprotokoll nicht über den Offenbarungsgehalt der internationalen Anmeldung im Anmeldezeitpunkt hinausgeht, wurde vorgelegt.
- ☐ Die Erklärung, daß die in computerlesbarer Form erfassten Informationen dem schriftlichen Sequenzprotokoll entsprechen, wurde vorgelegt.

4. Aufgrund der Änderungen sind folgende Unterlagen fortgefallen:

- ☐ Beschreibung,              Seiten:
- ☐ Ansprüche,                Nr.:
- ☐ Zeichnungen,            Blatt:

# INTERNATIONALER VORLÄUFIGER PRÜFUNGSBERICHT

Internationales Aktenzeichen PCT/EP00/08923

5. ☐ Dieser Bericht ist ohne Berücksichtigung (von einigen) der Änderungen erstellt worden, da diese aus den angegebenen Gründen nach Auffassung der Behörde über den Offenbarungsgehalt in der ursprünglich eingereichten Fassung hinausgehen (Regel 70.2(c)).

*(Auf Ersatzblätter, die solche Änderungen enthalten, ist unter Punkt 1 hinzuweisen; sie sind diesem Bericht beizufügen).*

6. Etwaige zusätzliche Bemerkungen:

## V. Begründete Feststellung nach Artikel 35(2) hinsichtlich der Neuheit, der erfinderischen Tätigkeit und der gewerblichen Anwendbarkeit; Unterlagen und Erklärungen zur Stützung dieser Feststellung

### 1. Feststellung

Neuheit (N)	Ja: Ansprüche	3-17
	Nein: Ansprüche	1,2
Erfinderische Tätigkeit (ET)	Ja: Ansprüche	3-17
	Nein: Ansprüche	
Gewerbliche Anwendbarkeit (GA)	Ja: Ansprüche	1-17
	Nein: Ansprüche	

2. Unterlagen und Erklärungen  
**siehe Beiblatt**

## VI. Bestimmte angeführte Unterlagen

1. Bestimmte veröffentlichte Unterlagen (Regel 70.10)

und / oder

2. Nicht-schriftliche Offenbarungen (Regel 70.9)

**siehe Beiblatt**

**zu Punkt V**

Von den im internationalen Recherchenbericht genannten Dokumenten wird auf folgende Dokumente Bezug genommen:

D1: US-A-5 490 980

D2: GARDENER, JOHN M, ET AL.: 'An investigation into the action of transglutaminase on human hair' J.SOC.COSMET.CHEM., Bd. 46, Nr. 1, Februar 1995 (1995-02), Seiten 11-28

*Neuheit, Artikel 33(2) PCT*

1. D1 beschreibt ein Verfahren zum Aufbringen einer aktiven Komponente auf menschliches Haar, wobei eine Zusammensetzung verwendet wird, die neben Transglutaminase einen für dieses Enzym substrataktiven Wirkstoff enthält (vgl. Ansprüche 6 und 1). Dieser Wirkstoff ist aus einer Gruppe auszuwählen, zu der auch Färbemittel gehören (vgl. Anspruch 3; col.7, Zeile 64 bis col.8, Zeile 18).  
  
D1 offenbart somit ein Verfahren das unter den breiten Wortlaut des unabhängigen Anspruchs 1 und des abhängigen Anspruchs 2 fällt. Diese Ansprüche können daher nicht als neu betrachtet werden.
2. Die zusätzlichen Merkmale der abhängigen Ansprüche 3-13 in Kombination mit dem unabhängigen Anspruch 1 sind in keinem der Dokumente des internationalen Recherchenberichts offenbart. Sie erfüllen somit die Erfordernisse des PCT in bezug auf Neuheit.
3. Die Gegenstände der zusätzlichen unabhängigen Ansprüche 14-17 sind ebenfalls nicht in den Dokumenten des internationalen Recherchenberichts offenbart und daher ebenfalls als neu zu betrachten.

*Erfinderische Tätigkeit, Artikel 33(3) PCT*

1. In D1 werden aktive Komponenten mittels dem Enzym Transglutaminase an menschliche Haut, Haare und Nägel gebunden.

D2 untersucht das Verhalten von Transglutaminase auf menschlichen Haaren; z.B. bildet Transglutaminase mit Proteinen eine vernetzte Schicht aus, die das Haar schützend umgibt.

2. In keinem dieser Dokumente ist jedoch erwähnt oder gibt es einen Hinweis, daß das Aufbringen von Transglutaminase zusammen mit einem substrataktiven Wirkstoff (z.B. Proteinen) einen verbessernden Einfluß auf die Waschechtheit von gefärbten Keratinfasern, insbesondere Haaren, hat.

Der Gegenstand der unabhängigen Ansprüche 14-17 sowie der abhängigen Ansprüche 3-13 beruht somit auf einer erfinderischen Tätigkeit.

**zu Punkt VI**

Das folgende Dokument wird beim Eintritt in das regionale Prüfungsverfahren als relevant betrachtet:

Veröff. No.:	WO-A-99/60200
Anm. No.:	PCT/US99/10496
Prio. Dat.:	20.05.1998 (US 09/082,218) 23.09.1998 (US 09/159,182)
Anm. Dat.:	12.05.1999
Veröff. Dat.:	25.11.1999